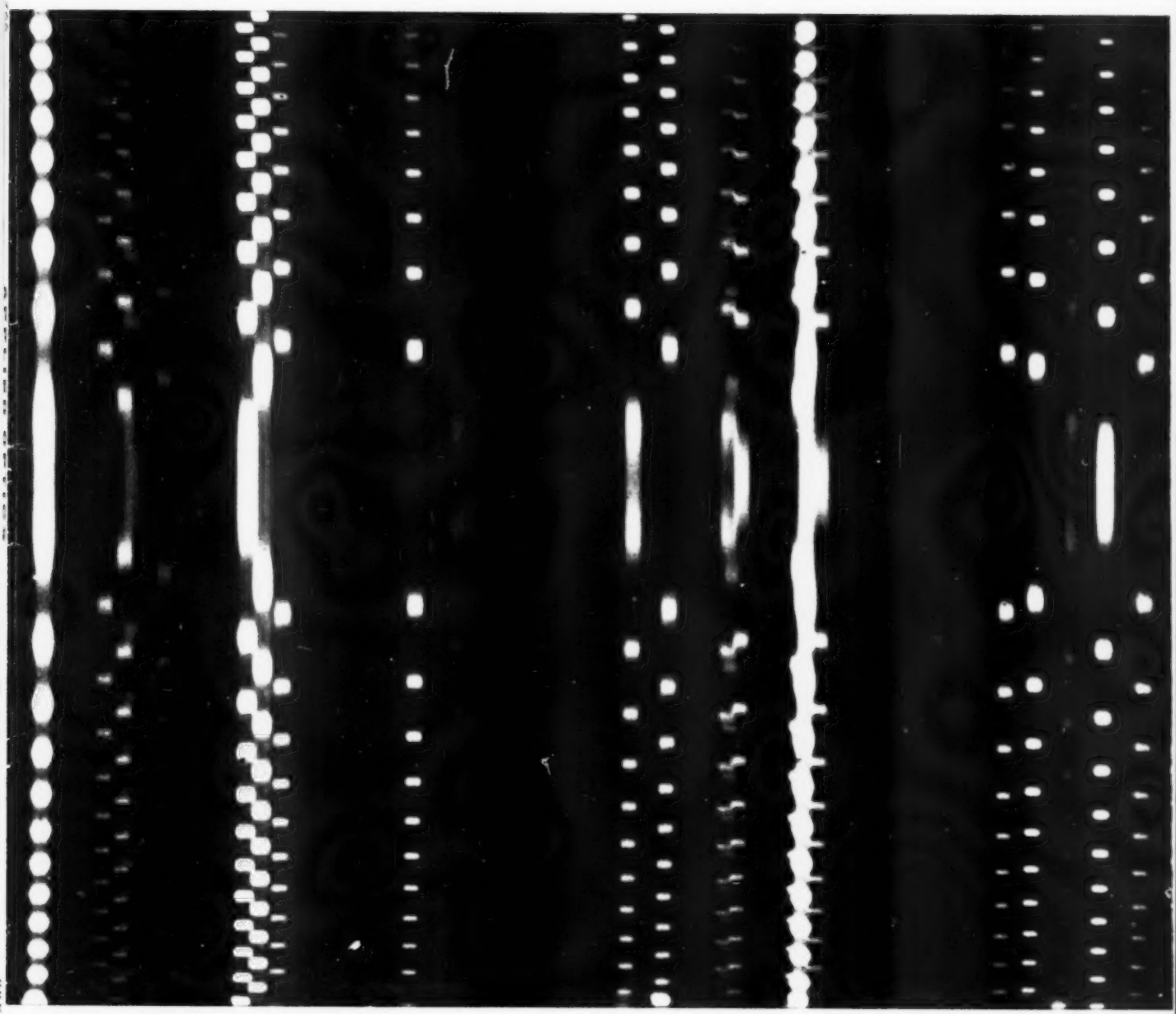
Applied Optics

July
1963



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VOLUME 2
NUMBER 7
JULY
1963

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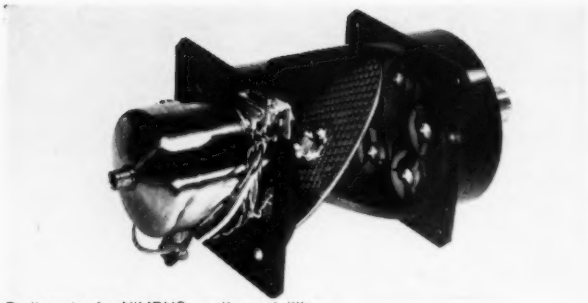
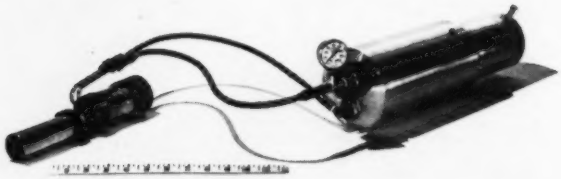
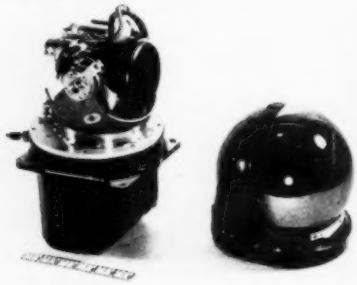


Radiometer for NIMBUS weather satellite

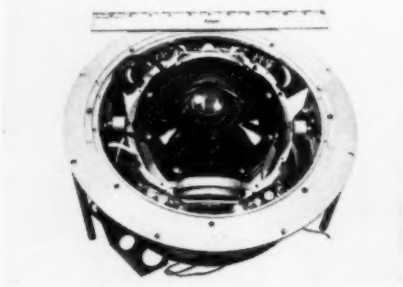
Interceptor IR installation



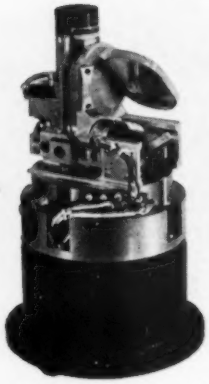
12°K closed-cycle cryostat



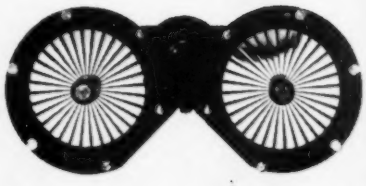
90C IR search/track set



IR multi-channel tracking radiometer



Star tracker for SURVEYOR spacecraft



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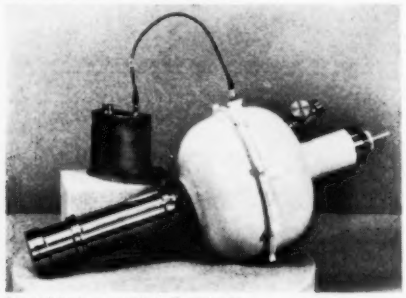

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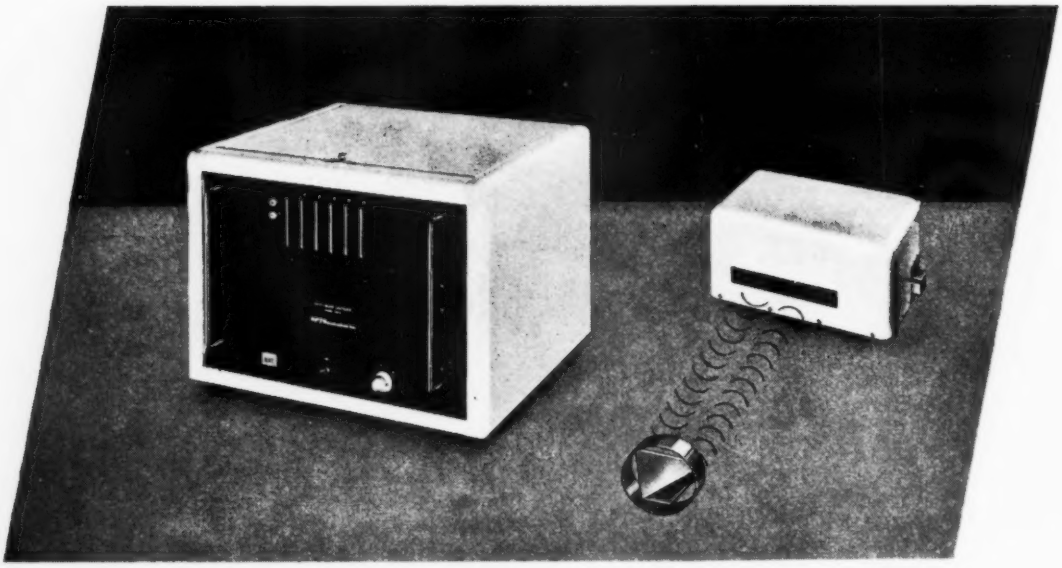

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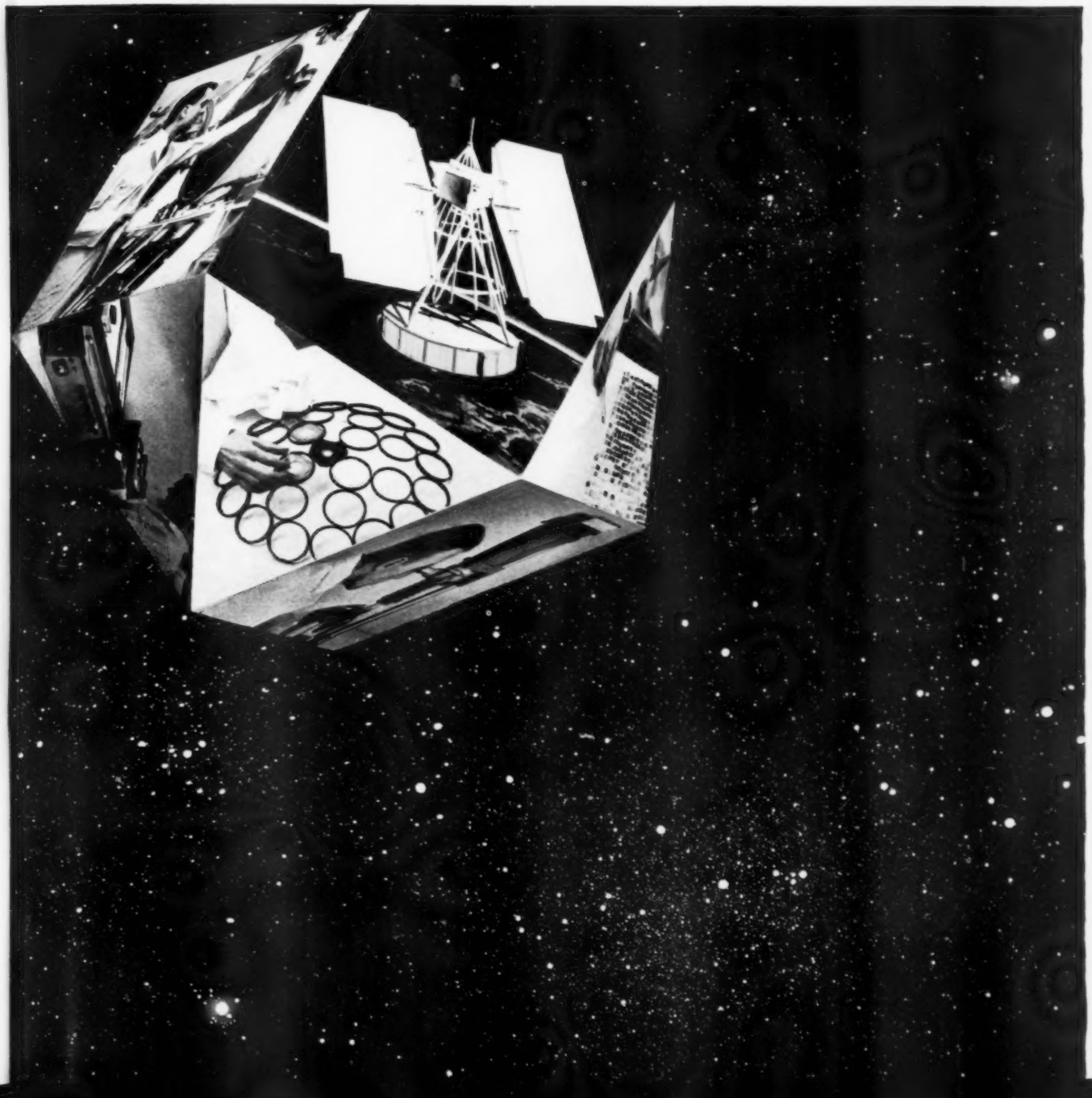

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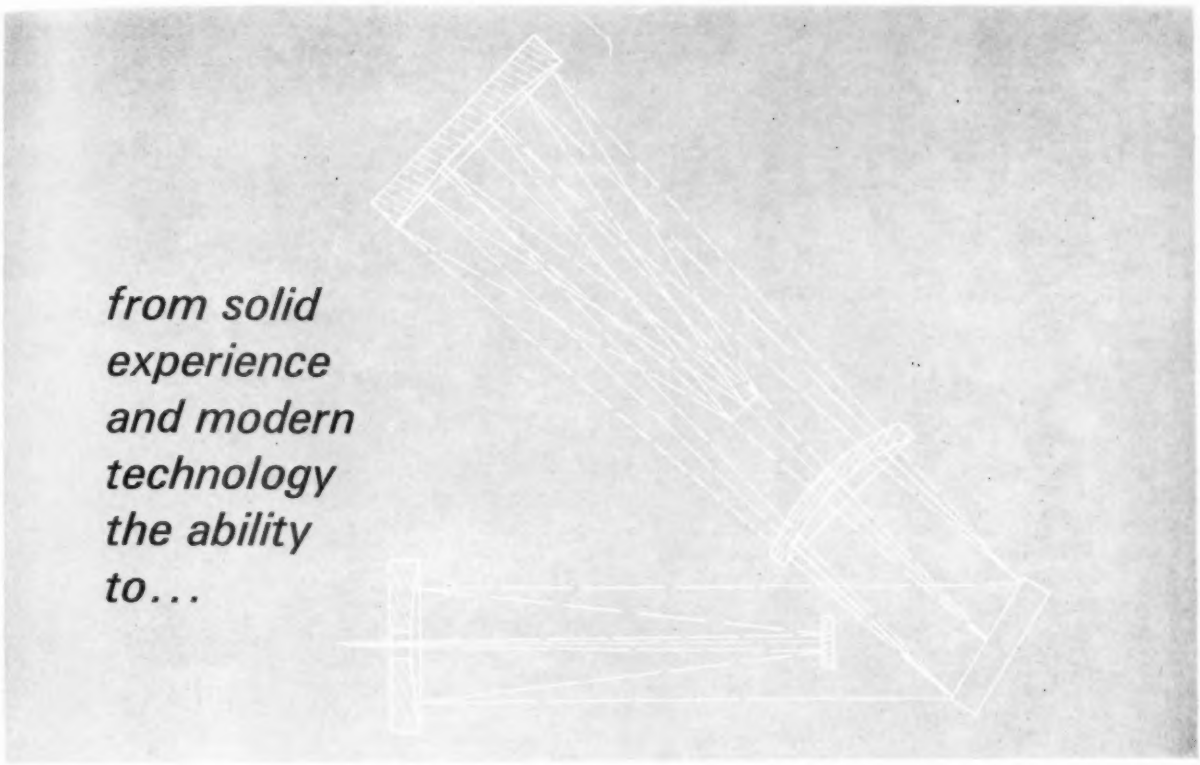

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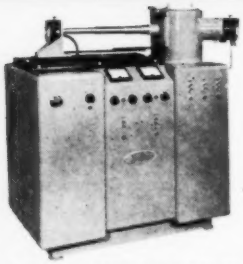

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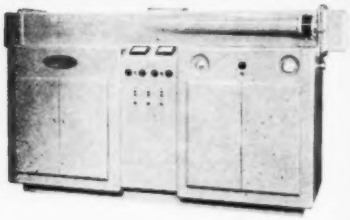

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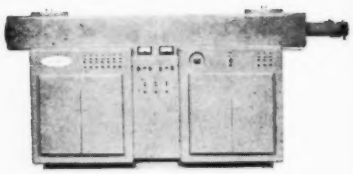

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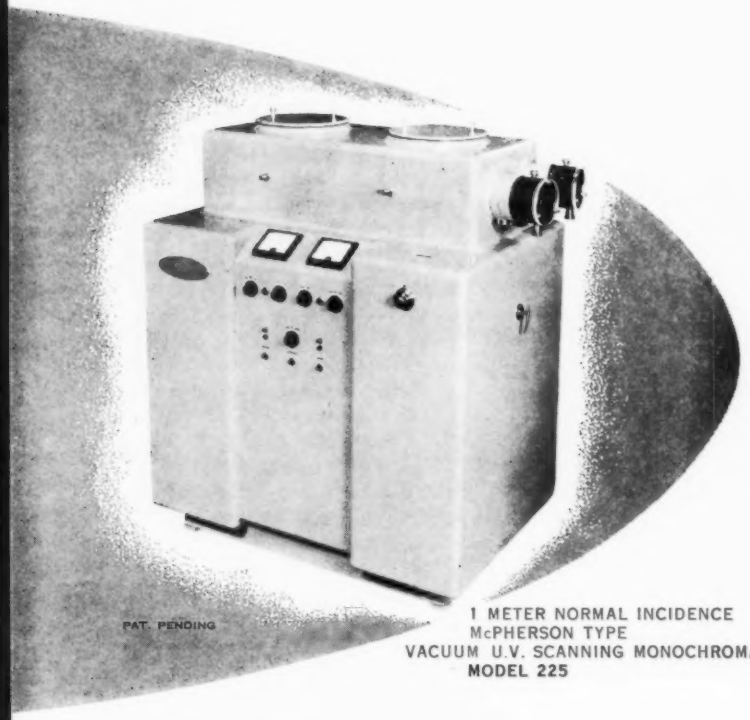

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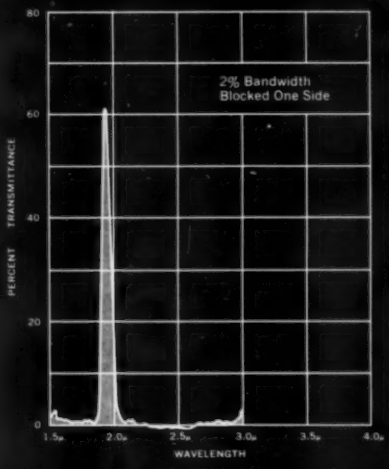

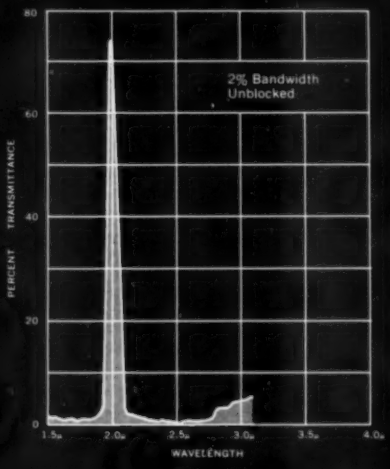

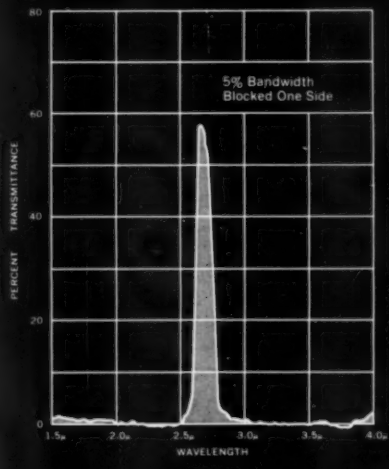

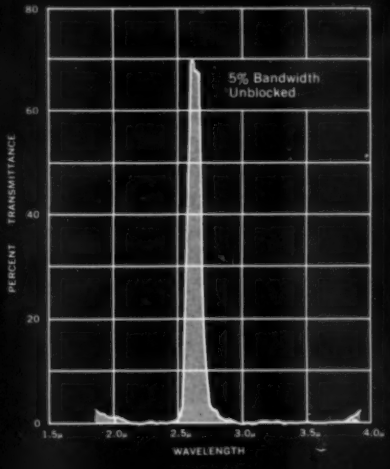

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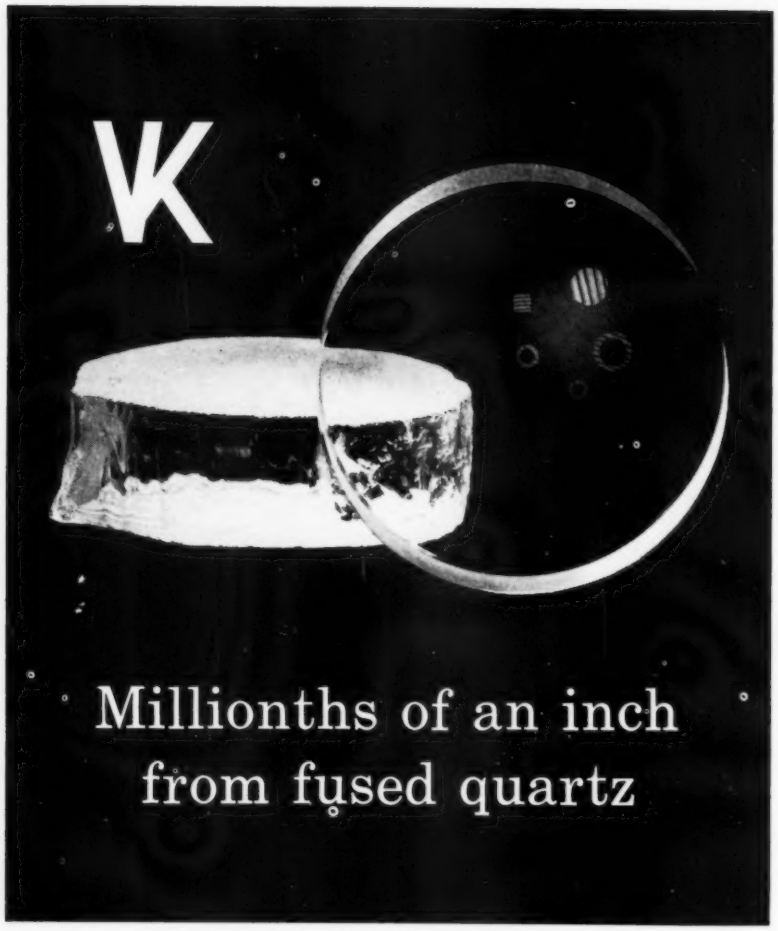

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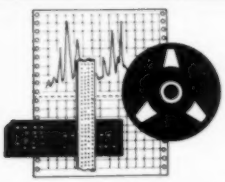

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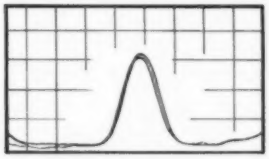

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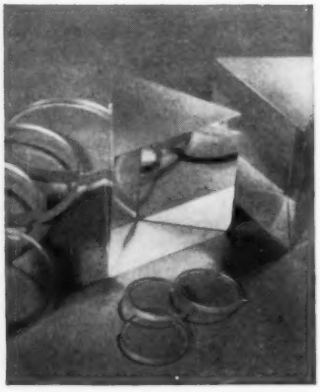

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Review of Reviews of Atomic Spectroscopy

William F. Meggers

In recent years there have been many references to the population explosion, including predictions of the year when there will be standing room only for human beings on the earth. There has been less publicity about the scientific explosion, but, in 1960, Wallace R. Brode said [Natl. Bur. Std. (U. S.) Monograph 43, Vol. I, pp. 1–4, (1962)], "The growth in number of scientists and engineers and the production of technical papers has been increasing at the rate of 10% per year with a doubling every 8 years, rather than doubling every 50 years as does the population . . . . As much has been published in the past 10 years as in the preceding time since the discovery of the printing press, and it is a well-quoted phrase that 90% of all the scientists who have ever existed are alive today." If this trend continues, and if we knew the present annual mass of scientific literature, we could predict the year in which the total accumulation of scientific papers will exceed the mass of the earth!

Seriously, scientists are painfully aware of the publication explosion and are trying to do something about it. For example, a 1960 progress report of the AIP Documentation Research Project states [Phys. Today **13** (No. 10), 42 (1960)]: "One of the major problems facing the physicist today is that of finding enough time and energy to keep up with the technical literature in areas of research in which he is involved. Some measure of his dilemma may be understood simply in terms of the rising abundance of reading matter in physics. In 1950, the American Institute of Physics and its Member Societies published 13,672 journal pages; in 1959, 23,022 pages were published, not including the Soviet translation journals and *Physical Review Letters*." In that report, it is shown that the number of abstracts in major physics abstract journals (*Physics Abstracts*, *Nuclear Science Abstracts*, *Physikalische Berichte*, and *Referativnyi Zhurnal Fizika*) increased from 48,660 in 1954 to 80,580 in 1959—an increase of 65% in 5 years, or an average of 10% per year.

In addition to the deluge of papers on classical and modern science in long-established journals, there has been a spectacular increase in number and variety of scientific periodicals; the present one, *Applied Optics*, was founded in 1962. In 1910 the library of the National Bureau of Standards received 234 journals presenting current literature in physics, chemistry, engineering, and mathematics; today, it accretes more than 2000 periodicals on these subjects, and storage space with accessibility has become its principal problem.

Obviously, if students, researchers, and technologists individually had to search the recent vast literature for items of interest or value, they would have little time for other activities. This situation justifies the publication of review articles on specific subjects, such as atomic spectroscopy; and, indeed, many such reviews have been made, especially since World War II. In fact, it is now impossible to prepare a condensed, comprehensive review of all atomic spectroscopy; the time appears ripe for a review of recent reviews.

Although modern atomic spectroscopy first really began to pay dividends about a half-century ago, after (1) the introduction of improved standards of wavelength and spectral-line intensities, (2) the quantum interpretation of line spectra and atomic structure, (3) improvements in spectroscopic apparatus and light sources, and (4) practical applications to quantitative chemical analysis, this paper will begin with reviews since 1946. In addition to the above content in easily accessible reviews, this paper will mention a few recent developments not mentioned in others. However, it will be restricted to the observation, interpretation, and application of line spectra associated with the outer electrons of atomic and ionic systems; specifically excluded are roentgen spectra, beta-ray and gamma-ray spectra, nuclear magnetic resonance spectroscopy, and quantum mechanics. Moreover, this paper will not mention all previous reviews, because those not specifically referred to are quite likely to be listed in other reviews.

Standard Wavelengths and Spectral-Line Intensities

Recent contributions to standard wavelengths have been succinctly summarized in the *Transactions of the*

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International Astronomical Union, which contains brief reports of its Commission on Standard Wavelengths and Spectral Tables. Thus, the 1948 report [Trans. I.A.U. **7**, 146–154 (1950)] contains a summary of nine directly measured values of the wavelength of the red line of cadmium in terms of the international meter; happily, the mean of all was identical with the value (6438.4696 Å) internationally adopted in 1907 to define the angstrom and serve as primary standard for spectroscopic measurements of wavelengths. Attention was also drawn to artificial Hg^{198} and separated Kr^{86} as sources of a primary standard superior to the Cd line. That report quoted interferometric measurements of 75 red and infrared wavelengths (6750.158 Å to 8999.562 Å) of the iron arc in air and 23 of neon (7059.109 Å to 8865.757 Å).

The report of the 1952 meeting [Trans. I.A.U. **8**, 188–198 (1954)] included five preliminary values of the wavelength of Hg^{198} green light in the same units as Cd red light; none deviated from the mean (5460.7532 Å) by more than 0.0001 Å. Interferometric values of 197 wavelengths (3369.808 Å to 8919.499 Å) from neon were compiled; the dispersion of air and tables of solar and atomic spectra were discussed; and the need for true line intensities, f values, or transition probabilities was stressed.

The report of the 1955 meeting [Trans. I.A.U. **9,** 201–227 (1957)] announced the appointment, by the International Committee on Weights and Measures, of an Advisory Committee on Redefining the Metre, which in 1953 recommended that the meter be defined by the wavelength of a luminous radiation *in vacuo*, that radiation being specified by two spectral terms of an atom whose spectrum is free from hyperfine structure and which is not subject to any perturbing influence. This I.A.U. report also presented interferometer values of 60 wavelengths (3351.7492 Å to 8082.4580 Å) from neon and 60 analogous values (3947.5046 Å to 11488.108 Å) from argon. Furthermore, the secondary standards of wavelength emitted by an iron arc in air were improved in accuracy and number by deriving from 575 interferometrically measured wavelengths (2501 Å to 9372 Å) the best values of 55 even and 138 odd atomic-energy levels and then calculating the wavelengths of 1016 permitted combinations ranging from 2084.1218 Å to 11973.067 Å. This list replaced all the iron standards previously adopted. These I.A.U. *Transactions* also contain a useful report of the Subcommission on Intensity Tables, including about 100 references to recent books and papers.

Considerable progress with standard wavelengths was reported at the Moscow meeting in 1958 [Trans. I.A.U. **10,** 211–233 (1960)]. At its second meeting in September 1957, the Advisory Committee on Redefining the Metre arrived at the unanimous recommendation that the meter be defined as exactly 1,650,763.73 wavelengths *in vacuo* of the radiation corresponding to the transition $2p_{10}$–$5d_5$ in krypton of mass number 86. The vacuum wavelength of this radiation is 6057.80211 Å relative to 6438.4696 Å of cadmium radiation in standard air. Preliminary values of 22 wavelengths (4275.1716 Å to 6458.0717 Å) were compiled for Kr^{86} radiations *in vacuo* relative to 6057.80211 Å. Provisional wavelengths (2457.5975 Å to 5709.3778 Å in standard air) of 283 iron lines emitted by low-pressure sources (hollow-cathode and electrodeless lamps) were also compiled.

Wavelength standards in the vacuum ultraviolet, where no interferometric measurements have been made, are obtainable with high precision from theoretical series calculations or from combinations between energy levels derived from interferometric measurements of longer waves. As examples of the first kind, the calculated wavelengths for the first six Lyman lines of nine elements from hydrogen through oxygen are presented; these range from 14.5243 Å to 1215.6701 Å. Of standards calculated on the combination principle, the following are assembled: 16 wavelengths of Hg^{198} spanning 1207.3784 Å to 1849.4918 Å, 29 of germanium ranging from 1691.6253 Å to 1998.8870 Å, 18 of Mg II between 946.7032 Å and 1753.474 Å, and 13 of Ca II between 1341.889 Å and 1850.691 Å.

The Subcommission on Intensity Tables reported on recent experimental and theoretical determinations of f values and listed general surveys, concise summaries, and about 100 references to literature on transition probabilities since 1955.

In supplementary tables, provisional vacuum wavelengths (4264.4849 Å to 6458.0718 Å) of 37 lines of Kr^{86} and of 4 lines of Hg^{198} (4358.3375 Å to 5792.2685 Å) were presented, and calculated wavelengths in standard air were published for 106 lines of neon (7051.2923 Å to 17164.94 Å) and for analogous lines of argon (8874.799 Å to 32297.09 Å). In addition, the number of calculated germanium standards for vacuum spectroscopy was increased from 29 to 75 spanning 1630.173 Å to 1998.8870 Å.

During the most recent meeting of the I.A.U., it was reported [Trans. I.A.U. **11A,** 97–130 (1962)] that, following the recommendation of the Advisory Committee on Redefining the Metre, the Eleventh General Conference of Weights and Measures, on 14 October 1960, unanimously adopted a resolution defining the meter as the length equal to 1,650,763.73 wavelengths *in vacuo* of the radiation corresponding to the transitions between the $2p_{10}$ and $5d_5$ levels of the krypton-86 atom. The reciprocal of this number gives the wavelength 6057.80211 Å, and the angstrom is simply 10^{-10} m. That wavelength thus became the international standard of length as well as the primary standard of wavelength; this is an outstanding example of *Applied Optics* (see cover illustration of this journal).

The development of an Hg^{198} atomic-beam light source and demonstration that it emitted much sharper lines than Kr^{86} [R. L. Barger and K. G. Kessler, J. Opt. Soc. Am. **50,** 651–656 (1960)] came too late to compete as a primary standard of length; when greater precision is needed, it will probably be found in a gaseous laser, now being developed.

A rigid review of "The International Length Standards" by K. M. Baird and L. E. Howlett appeared in the May issue of this journal [Appl. Opt. **2,** 455–463 (1963)], and recent progress in the techniques of calibrating ruled line standards by interferometry was reviewed by K. M. Baird, "Interference Comparators for Line Standards", in the same issue [Appl. Opt. **2,** 471–479 (1963)].

In the above-mentioned I.A.U. report [Trans. I.A.U. **11A,** 97–130, (1962)] appear further compilations of Class A Secondary Standards, represented by 7 lines of Kr^{86}, 7 of Hg^{198}, and 4 of Cd^{114}. Under Class B Secondary Standards, additional determinations of vacuum wavelengths of iron lines at low pressure are reported, and observed vacuum wavelengths of 432 thorium lines (2566.3615 Å to 9050.7361 Å) emitted by low-pressure lamps are compiled for the first time.

Observed vacuum wavelengths in the infrared are collected for 6 lines of Hg^{198} (from 10142.572 Å to 15300.152 Å) and 12 lines of Kr^{86} (from 7603.6337 Å to 16789.722 Å). For the vacuum-ultraviolet region, standards based upon the combination principle have been computed for 223 lines appearing in the Ar II, C I, C II, O I, N I, and Cu II spectra; the wavelengths range from 487.2274 Å to 1989.8541 Å.

Meticulous measurements of wavelengths, energy levels, and pressure shifts from Meggers mercury-198 lamps have been reported by V. Kaufman [J. Opt. Soc. Am. **52,** 866–870 (1962)], who measured the vacuum wavelengths of 25 lines of Hg^{198} (2537.2688 Å to 5792.2683 Å) and 6 of Kr^{86} (5563.7690 Å to 6084.5440 Å), all relative to the new primary standard, 6057.80211 Å of Kr^{86}.

From interferometric measurements of Ge I and Ge II wavelengths (2019 Å to 12,069 Å), V. Kaufman and K. L. Andrew [J. Opt. Soc. Am. **52,** 1223–1237 (1962)] calculated about 100 germanium vacuum ultraviolet Ritz standards (999.1003 Å to 1998.8869 Å), 68 of which have estimated uncertainties of 0.0003 Å.

All of the above information concerning standard wavelengths in the vacuum region is summarized and superseded by B. Edlén's recent report, "Wavelength Measurements in the Vacuum Ultraviolet" [Repts. Prog. Phys. **26** (1963)], in which recording technique, light sources for vacuum-ultraviolet atomic spectra, evaluation of spectrograms, and wavelength standards are discussed in detail.

The most interesting and useful survey of "The Extreme Ultraviolet—Past and Future" has been given by R. Tousey [Appl. Opt. **1,** 679–694 (1962)], who begins with the discovery of the extreme ultraviolet and discusses the period from 1915 to 1930, solution of the problem of the coronal lines, the post-1945 period, mountings for grating monochromators, reflecting coatings, filters, diffraction gratings, light sources, photographic films, photoelectric detectors, photon counters and ion chambers, space research, plasma spectroscopy, and other applications, and includes a bibliography of 13 books and 143 literature references.

In the most recent I.A.U. reports, there are 90 references to papers about standard wavelengths and atomic spectra published between 1957 and 1961; during the same time, nearly 200 were published dealing with transition probabilities, continuous absorption, forbidden lines, molecules, and cross sections for excitation and ionization of electrons. The massive *Tables of Spectral-Line Intensities* prepared by W. F. Meggers, C. H. Corliss, and B. F. Scribner [Natl. Bur. Std. (U.S.) Monograph 32, Part I, Arranged by Elements, 473 pp.; Part II, Arranged by Wavelengths, 271 pp. (1961)], should also be mentioned. These *Tables* contain wavelengths (2000 Å to 9000 Å) and calibrated intensities for 39,000 spectral lines emitted by 70 metallic elements when diluted a thousandfold in copper and burned in a dc arc. Altogether, the strong lines of 120 spectra (I, II, III) of these elements are represented, and the atomic- or ionic-energy levels responsible for them have been supplied for nearly 25,000 lines. It appears that these *Tables* contain the first quantitative-intensity data for about one-half of the investigated elements.

In *Experimental Transition Probabilities for Spectral Lines of Seventy Elements* [Natl. Bur. Std. (U.S.) Monograph 53, 562 pp. (1962)], C. H. Corliss and W. R. Bozman have derived and assembled the physical quantities and calibration functions necessary to calculate transition probabilities and oscillator strengths on an absolute scale from the intensity numbers in the NBS *Tables of Spectral-Line Intensities.* The calculations have been performed, and the results are tabulated for 25,000 lines from 112 spectra of 70 elements. The particular significance of these results lies in the large number of values made available, the long range of wavelengths encompassed, the inclusion of many lines from singly ionized atoms and from elements not previously investigated, the use of a uniform scale, and the fact that the scale is absolute.

The most complete and up-to-date of its kind, *Bibliography on Atomic Transition Probabilities* containing references to more than 600 papers, has been prepared by B. M. Glennon and W. L. Wiese [Natl. Bur. Std. (U.S.) Monograph 50, 42 pp. (1962)].

One supplementary paper comes to mind—it reports

relative intensities and *gf* values for 180 lines of Cu I, between 2600 Å and 7200 Å, observed in a 10-A copper arc [C. H. Corliss, J. Res. Natl. Bur. Std. **66A,** 497–502 (1962)].

The Quantum Interpretation of Line Spectra

In 1946, I briefly reviewed "Spectroscopy, Past, Present, and Future" [J. Opt. Soc. Am. **36,** 431–448 (1946)], with emphasis on two decades of research on the fine structure and hyperfine structure of optical spectra and the rebirth of spectrochemistry. Two earlier reviews were cited, and 378 research papers were listed as contributing to the quantum interpretation of 445 spectra of 77 elements and to the nuclear moments of 91 isotopes belonging to 63 atomic species. That year, Charlotte E. Moore began to compile and publish *Atomic Energy Levels as Derived from the Analyses of Optical Spectra,* which has resulted thus far in the issuance of three classical reviews of the world's literature on the fine structure of atomic and ionic spectra and supplementary *Multiplet Tables.* Volume I of *Atomic Energy Levels* [Natl. Bur. Std. (U.S.) Circular 467, 309 pp. (1949)] presented results for 206 spectra of the first 23 elements, 1 H through 23 V; Volume II [Natl. Bur. Std. (U.S.) Circular 467, 227 pp. (1952)] gave similar data for 152 spectra of the next 18 elements, 24 Cr through 41 Nb; and Volume III [Natl. Bur. Std. (U.S.) Circular 467, 245 pp. (1958)], reports on 124 spectra of 32 elements, 42 Mo through 57 La and 72 Hf through 89 Ac.

Because relatively little is known about the term structure of spectra emitted by "rare earths," 58 Ce through 71 Lu and 90 Th through 103 Lu, no compilation of comparable data exists, but sufficient progress has been made in describing and analyzing these spectra to justify the hope that some results will be presented in Volume IV of *Atomic Energy Levels* in the near future, provided adequate manpower is applied. In the meantime, regular reports on the status of research in atomic spectroscopy have been supplied by the Joint Commission for Spectroscopy [J. Opt. Soc. Am. **41,** 143–148 (1951); *Ibid.* **43,** 410–430 (1953); *Ibid.* **46,** 145–149 (1956); *Ibid.* **47,** 1035-1041 (1957); *Ibid.* **50,** 396–417 (1960)] and more recently by the Triple Commission for Spectroscopy [J. Opt. Soc. Am. **52,** 473–483 (1962); *Ibid.* **52,** 583–584 (1962); *Ibid.* **53,** 883–893 (1963)]. Furthermore, the present status of first and second spectra of rare-earth elements is reviewed in this journal [Appl. Opt. **2,** 667–674 (1963)] by Charlotte E. Moore and the third and fourth spectra of these elements in this same journal [Appl. Opt. **2,** 675–686 (1963)] by G. H. Dieke and H. M. Crosswhite.

The material in the first three volumes of *Atomic Energy Levels* inspired Bengt Edlén to make the most extensive and elegant review of atomic spectra [*Handbuch der Physik,* S. Flügge ed. (Springer-Verlag, Berlin, 1963), Vol. 27]. That review is concerned with the undisturbed gross structure of the energy-level systems of free atoms and ions, the main content being a description of relationships between different, especially isoelectronic, systems. This gives a survey of empirical data in a form useful to the theorist and at the same time provides the experimentalist with a collection of theoretical results for direct application and with efficient methods for the analysis and description of his observations. A considerable part of this material, in particular on isoelectronic sequences, has not been previously published. In five chapters, Edlén has presented (1) basic concepts, (2) relative term values of many-electron configurations, (3) absolute term values and properties of Rydberg series, (4) isoelectronic sequences, and (5) regularities along periods. The results are shown in 70 tables (of integrals, parameters, functions, intervals, ionization energies, and the like) and 80 line figures.

Since atomic-energy levels are affected in perfectly predictable ways by magnetic fields, the Zeeman effect became one of the most powerful aids in the analysis of spectra. The history and theory of the Zeeman effect (based on the vector model) have been reviewed by J. C. van den Bosch [*Handbuch der Physik,* S. Flügge ed. (Springer-Verlag, Berlin, 1957), Vol. 28, pp. 296–332].

The main result of this review of recent reviews of atomic spectroscopy is that the ground state and electron configuration have been experimentally determined for all neutral atoms from 1 H to 96 Cm, except 85 At and 87 Fr, whose spectra have not been investigated. The same may be said for nearly all singly ionized atoms from 2 He to 95 Am, but the spectra of more doubly ionized and of most higher-ionized atoms still await investigation. Incentives for doing this are now found in pure materials, improved light sources and spectrographs, automation, and demands of modern astrophysics and plasma physics for more information about the higher spectra of atoms in general. It is certain that interesting spectrographic results have been obtained with nuclear explosives as light sources, but this author knows of no published review of these experiments.

For more than three decades, the derivation of nuclear moments (mechanical, magnetic, and electric quadrupole) from hyperfine structure of spectral lines has paralleled the activity of deriving atomic structure from spectra, and recent development of radio-frequency spectroscopy has provided new methods (nuclear magnetic resonance, nuclear quadrupole resonance, and paramagnetic resonance) of attack that far surpass optical instruments in resolving power. Certain quantum numbers deduced from the term structure of a spectrum are usually prerequisite to the interpretation of hyperfine structure. This subject

is complicated because, in the case of elements with several isotopes, a reliable analysis of the hyperfine structure is impossible without a detailed examination of the isotope shift, the exclusive domain of optical interference spectroscopy. Apart from that, the isotope shift furnishes information on the change of the nuclear charge distribution from isotope to isotope as well as on the quadrupole moments of strongly deformed nuclei. Indeed, results on the isotope shift have given the first indication that nuclei with zero spin may be deformed.

A compact review of determination of nuclear spins and magnetic moments by spectroscopic methods by F. M. Kelly [*Handbuch der Physik*, S. Flügge ed. (Springer-Verlag, Berlin, 1958), Vol. 28, pp. 59–95] and the article on isotope shifts by L. Wilets (*Ibid.*, pp. 96–119) discuss methods of observing and theory of origin, but they omit most results.

All reviews of nuclear moments preceding 1955 were superseded by H. Kopfermann's book, *Kernmomente*, and that book in turn by the expanded English edition called *Nuclear Moments*, prepared in 1957 by E. E. Schneider (Academic Press, New York, 1958). Incidentally, the latter book was reviewed in *Physics Today* **11** (No. 11), 36 (1958). Another review of nuclear data of the same date was published by K. F. Smith [Progr. in Nuclear Phys. **6**, 81–87 (1957)], but I am not aware of a more recent compilation. In 1946, I compiled mechanical moments, I, for 90 atomic nuclei, magnetic moments, μ, for 70, and quadrupole moments, Q, for 20. In 1957, K. F. Smith compiled I values for 227 nuclides, μ for 195, and Q for 79; the number now known is unknown unless someone has taken the time to count them in the world's prolific literature on atomic and nuclear physics.

Improvements in Spectroscopic Apparatus and Light Sources

In 1944, a unique book on *Experimental Spectroscopy* was published [R. A. Sawyer (Prentice-Hall, New York 1944), 323 pp.; enlarged second edition (1951), 358 pp.] and reviewed [W. F. Meggers, Science **100**, 385–386 (1944)]. That book discussed prism and grating spectrographs but did not mention interferometers. In the succeeding years, prisms have been gradually displaced by ruled diffraction gratings, mainly on account of fundamental advantages of the latter for dispersing and resolving spectra and extensive activity in the production of concave and plane gratings.

Recent planning for the eventual establishment of space observatories above the earth's atmosphere has inspired T. Namioka [*Space Astrophysics*, (McGraw-Hill, New York, 1961), pp. 228–268] to review various grating mountings suitable for a monochromator in a space telescope. Following a review of the theory of the concave grating (both spherical and ellipsoidal), 11 different grating mountings are described and discussed, supplemented by 63 literature references.

Efforts to resolve hyperfine structures and isotope shifts in atomic spectra have resulted in some important improvements in optical interferometers and some good books on this subject. See *Modern Interferometers* by C. Candler (Hilger & Watts, London, 1951), reviewed by W. F. Meggers [J. Opt. Soc. Am. **41**, 1064 (1951)]. *High-Resolution Spectroscopy* by S. Tolansky [(Methuen, London, 1947) 285 pp.] contains a bibliography of 128 items; it describes in detail the experimental technique of combining sharp-lined light sources (Geissler tubes, electrodeless discharges, hollow cathodes, atomic beams) with interferometers (Fabry-Perot, Lummer plate, and Michelson echelon) to obtain the maximum resolving power of spectral details. *An Introduction to Interferometry* by S. Tolansky (Longmans, Green, New York, 1955) was written especially for students; it appears to be unique in the field of scientific pedagogy.

New developments in interference spectroscopy have been reviewed in detail by P. Jacquinot [Repts. Progr. Phys. **23**, 268 (1960)]. "After an introduction (Part I) dealing with the different possibilities of classifying the methods of interference spectroscopy, Part II deals with the more recent developments in Fabry-Perot spectroscopy. A complete theory, including the role of surface imperfections and of field diaphragm, is given, and the recent improvements in dielectric coating are reviewed. A complete outline of the photoelectric use of the Fabry-Perot is given, including methods of scanning for low and high resolutions, best compromise between luminosity and resolution, and calculation of the luminosity and extensions of the Fabry-Perot method to studies of absorption spectra. The properties of a new spherical Fabry-Perot spectrometer are described. Some recent results obtained with photographic methods are briefly discussed. Part III deals with a new type of spectrometer which selects the different wavelengths by the *amplitude* of the modulation given to them by a linear variation of the optical path. Such an instrument, using gratings, for instance, is capable of yielding the same resolution as would be obtained if one of the gratings was used in a conventional fashion with very narrow slits, but it provides a much higher luminosity. Part IV deals with methods of selecting the different wavelengths by the *frequency* of their interferometric modulation: the spectrum is not given in the usual form, but in the form of interferogram, which is the Fourier transform of the spectrum. The main advantage of these methods is that, in common with the photographic method, the time required for recording the interferogram does not depend upon the width of the spectrum studied. The resolving power and the luminosity of the process are studied. Some methods

of application are described as are the different methods of reconstitution of the spectrum from the interferogram. Some recent applications of Michelson's method of 'visibility of fringes' are also reviewed." That review includes 98 references to other publications, 87 since 1950.

In a discussion of the "Quantum Limit to Precision of Wavelength Determination", G. R. Hanes [Appl. Opt. **2,** 465–470 (1963)] has surveyed the theoretical precision capabilities of five different spectroscopic instruments: viz., prism, grating, Fabry-Perot interferometer, Michelson interferometer, and spherical Fabry-Perot interferometer.

Electrical arcs, high-voltage condensed sparks, Geissler tubes, high-frequency ring discharges, hollow-cathode lamps, and excited atomic beams are classical light sources for the investigation of spectra, familiar to all spectroscopists, but nobody has supplied a comprehensive modern review of them. In the present review of reviews, I can only refer to Tolansky's description in *High Resolution Spectroscopy* of the last four above mentioned as providing sharp lines for interferometric study, and Edlén's [Repts. Progr. Phys. **26** (1963)] brief description of sources, including the vacuum spark and vacuum sidling spark, suitable for producing spectra in the vacuum ultraviolet. The sliding vacuum spark was first suggested by B. Vodar and N. Astoin [Nature **166,** 1029–1030 (1950)] and has been successfully applied to the description of ionic spectra and to spectrochemical analysis because it permits easy control of ionization and excitation and produces sharper lines than a condensed discharge in a hollow cathode.

Another recent innovation in spectroscopic light sources is an electrodeless lamp consisting of a small quartz tube containing a gaseous or metallic sample excited by ultra-high frequency usually provided by a commercial magnetron. Regarding the Meggers Hg^{198} lamp as the prototype, others have shown [J. Opt. Soc. Am. **42,** 818–819 (1952)] that most metals with adequate vapor pressure are strongly excited and [*Ibid.* **43,** 398–400 (1953)] that metals with very high melting points also yield brilliant spectra if a volatile halide is used. These lamps are outstanding in simplicity, strength, and economy; they are especially useful for rare or radioactive elements because they operate with microgram samples and conserve them.

The first successful application of stimulated emission in an electronic amplifying device was made in 1954 with the invention of the maser (acronym for microwave amplification by stimulated emission of radiation). In 1960, a maser device was first operated in the visible spectrum; light replaced microwave, and maser became laser. Spectacular developments in lasers are providing new spectroscopic light sources with fantastic properties (intensity, directivity, monochromaticity, coherence), and it is not easy to keep abreast of progress. Fortunately, review papers are available, although the subject is barely two years old. Thus, the *Applied Optics* supplement on optical masers, published in 1962, contains a 23-page article, "Optical Masers", by O. S. Heavens, who discusses concepts basic to the understanding of these devices and summarizes the work on solid-state systems and applications to fundamental experiments, communications, instrumentation, and surgery found in 92 references. The second paper (38 pages and 41 references) by W. R. Bennett, Jr., gives a detailed review of the present knowledge of gaseous optical masers. It is stated that, in the first year of laser development, continuous oscillation had been obtained on over 40 different optical transitions, ranging from the visible (0.63 μ) through the middle infrared (12 μ), by using 10 different gas systems and at least 4 different excitation mechanisms. At least one book on this subject has already appeared; it is by Bela A. Lengyel and members of the technical staff of Hughes Research Laboratories [*Lasers* (Wiley, New York, 1962), 125 pp.]. A "Bibliography of the Open Literature on Lasers" [J. Opt. Soc. Am. **53,** 647–652 (1963)] lists 208 papers, all but 3 published since 1960. Here we may expect continuous spectroscopic explosions, and we will gratefully greet future reviews on lasers.

Applications to Quantitative Chemical Analysis

In 1946, it was stated [J. Opt. Soc. Am. **36,** 431–448 (1946)] that "parallel with the quantum-theoretical interpretation of atomic spectra there occurred a rebirth and phenomenal development of spectroscopy applied to chemical analysis. It is strange but undeniable that these two events have little in common except coincidence in time." Beginning with a paper entitled "Practical Spectrographic Analysis" in 1922 [Sci. Pap. Bur. Stand. **18,** 235–255 (1922)] and subsequent revival of spectrochemical analysis in the land of its birth, Gerlach and Schweitzer in 1926 published their *Chemische Emissions-Spektralanalyse.* This marked the beginning of a steadily increasing output of papers, now totaling perhaps 10,000, partly listed and abstracted in the four-part *Index to the Literature of Spectrochemical Analysis* [W. F. Meggers and B. F. Scribner (Am. Soc. Testing Mat., Philadelphia, 1941–1959)].

Naturally, this flood of papers invited the preparation of many reviews, among which only the series initiated by Meggers and continued by Scribner for *Analytical Chemistry* will be mentioned, because these contain references to all other reviews. Our intention was to select from the world output of spectroscopic literature noteworthy items concerning atomic spectra, their production, interpretation, and application, and publish them in a widely read journal as annual or

biennial reviews of emission spectroscopy. The following is a list of reviews thus far published in this series:

W. F. Meggers, "Emission Spectroscopy," Anal. Chem. **21**, 29–31, 1949, 64 refs.
W. F. Meggers, "Emission Spectroscopy," Anal. Chem. **22**, 18–23, 1950, 104 refs.
W. F. Meggers, "Emission Spectroscopy," Anal. Chem. **24**, 23–27, 1952, 139 refs.
W. F. Meggers, "Emission Spectroscopy," Anal. Chem. **26**, 54–58, 1954, 147 refs.
W. F. Meggers, "Emission Spectroscopy," Anal. Chem., **28**, 616–621, 1956, 99 refs.
B. F. Scribner, "Emission Spectroscopy," Anal. Chem. **30**, 596–604, 1958, 263 refs.
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The "explosion" of spectrochemistry is obvious everywhere. Heretofore, emission flame photometry had been included with emission spectroscopy, but now it rates its own review in *Analytical Chemistry*.

For more than two decades, there have been various sectional or national conferences on applied spectroscopy, and, in most cases, voluminous proceedings of such meetings have been published in the United States, Britain, France, Germany, the Soviet Union, Greater China, and perhaps elsewhere. Furthermore, the Xth Colloquium Spectroscopicum Internationale was held in June 1962 in the United States, and the XIth will occur in October 1963 in Yugoslavia. The bulky and monotonous proceedings of all these conferences and colloquia may be available to the industrious and conscientious spectrochemist, but before he tries to digest them all, we recommend that he consult brief reviews and relax, if necessary, by reading, for example: "Principals and Principles of Spectrochemical Analysis" [Spectrochim. Acta **3,** 5–17 (1947)] and "Centennial of Spectrochemistry" [J. Opt. Soc. Am. **50,** 1035–1038 (1960) and Richerche Spettroscopische **3,** 1–35 (1962)].

Probably accidentally, the centennial year of spectrochemistry witnessed the publication of the first *Encyclopedia of Spectroscopy* [George L. Clark ed. (Reinhold, New York, 1960) 787 pp.]. This volume reviews 20 types of spectroscopy, from absorption spectroscopy to x-ray spectroscopy, in 264 subtopics by 120 authors. The treatment is uniformly elementary, and the emphasis is on practical applications. The section titled "Emission Spectroscopy—Light" covers pages 99 to 330; it begins with accuracy in spectrochemical analysis and concludes with Zeeman effect. Because spectroscopy has proved to be a tool of great value in pure and applied optics, we may expect to see more reviews and encyclopedias in the future.

Meeting Reports

International Symposium on Far Infrared Spectroscopy, Cincinnati, Ohio, August 21–24, 1962

Reported by E. H. Siegler, Perkin-Elmer

The first major symposium to be held on this phase of infrared spectroscopy, this meeting was sponsored by the United States Air Force, and Freeman F. Bentley of Wright Field, the General Chairman, was responsible for the planning and organization which made it possible. The comment of one of the more than 250 participants was, "I thought I was working in a frontier, but look at all these people." The size of the meeting resulted not only from increasing interest in far infrared research but also from the diversity of topics covered. Quality was insured by the participation of leading far infrared scientists from many countries, such as H. A. Gebbie *National Physical Laboratory, England;* L. Genzel *University of Freiburg, Germany;* A. Hadni *University of Nancy, France;* J. Lecomte *Sorbonne, Paris;* R. C. Lord *MIT;* E. K. Plyler *National Bureau of Standards;* R. A. Smith *University of Sheffield, England;* and H. Y. Yoshinaga *Osaka University, Japan*. Col. L. R. Standifer, who gave the welcoming address, which opened the meeting, was the official Air Force representative to the banquet at which John N. Howard AFCRL was toastmaster, and R. Bowling Barnes, the guest speaker, delivered an entertaining description of far infrared spectroscopy in the "old days."

The technical program consisted of 30 invited papers covering various aspects of far infrared spectroscopy, and the emphasis in most papers was on the experimental rather than the theoretical side. The spectral region of interest was usually all or some part of the range from 660 cm^{-1} to 3 cm^{-1}. It is planned to publish a number of the papers in a future edition of *Spectrochimica Acta*. The first day was devoted to studies of molecular structure using far infrared. Bryce L. Crawford, Jr., *Minn.*, gave the keynote paper explaining why far infrared frequencies are of particular interest to molecular dynamics. He showed they are essential for complete vibrational assignment; they may affect higher frequencies quite significantly by resonance interaction; they are the motions involving the entire molecule rather than local groups, and hence contain information regarding the coupling forces within a molecule; and they provide some of the best tests for our understanding of force constants. Various chemical applications were discussed on the second day, and the papers included work on inorganic carbonates and nitrates, organosilicon compounds, benzene derivatives, phosphorous compounds, and biological materials. There were three papers which showed the usefulness of far infrared for studying the structure and crystallinity of polymers as well as for polymer identification. Six papers on the third day dealt with recent solid-state research employing far infrared spectroscopy. The spectra for a considerable number of crystals were shown and interpreted, and it was demonstrated that, in addition to elucidating crystal forces and structures, far infrared spectra provide much useful information concerning ferroelectric and antiferromagnetic materials, semiconductors, and superconductors. M. Tinkham, *California*, concluded that "Far infrared is a useful field for physicists as well as chemists to work in." The last papers were on far infrared instrumentation. These included discussion of a fast new InSb detector, Fabry-Perot interference filters as well as other filtering means, diffrac-

tion gratings, and a Golay detector filled with absorbing gas. Among the instruments described were a Michelson interferometer and two double-beam spectrometers.

Also, of course, there was extensive informal discussion which the meeting served to focus on the far infrared field. For example, Paul Richards *Bell Labs*, disclosed that ferrimagnetic resonance of ytterbium iron garnet at 3.0 cm^{-1} has been observed for the first time using his lamellar grating interferometer with a cooled doped germanium detector. He obtains 0.2 cm^{-1} resolution. R. A. Oetjen mentioned that satisfactory operation was being obtained with the interferometric modulator at Ohio State University.

The stated objective for the meeting was to promote the interchange of knowledge on current research in far infrared spectroscopy, both basic and applied. The meeting was clearly successful in meeting this objective. Moreover it served as a distinct milestone in the growth and progress of this increasingly active field.

International Symposium on Molecular Structure and Spectroscopy, Tokyo, Japan, 10–15 September 1962

Reported by M. Kent Wilson, Tufts University

This meeting, the first international symposium on spectroscopy held in Japan, was undoubtedly one of the best organized conferences any of the participants had attended. From the start of the plenary session on Monday to the end of the symposium excursion to Nikko on Saturday, the meeting was conducted with the precision of a fine optical instrument.

Four parallel sessions included topics in all phases of spectroscopy from the deep-ultraviolet to the radio-frequency region. Preprints of all papers including those presented during the plenary session and invited papers given during the week were available at registration. S. Mizushima *Tokyo* opened the plenary session with a review of the Japanese work on molecules exhibiting internal rotation. This presentation was followed by a paper by H. W. Thompson *Oxford* in which the current status of vibration-rotation spectra was discussed. His comments ranged from a consideration of the structural information obtainable from high-resolution spectra of small molecules to studies of molecular interactions in condensed phases. Considerable emphasis was placed on band contours as a source of information concerning specific intermolecular forces between molecules in solution. A talk by G. Herzberg *NRC-Canada* is a highlight of any spectroscopic meeting, and this meeting was no exception. Herzberg reviewed the work on the spectra of free radicals that has been completed or is under way at Ottawa, including the fascinating search for CH_2. This molecule exists in two forms: a linear variety that is probably triplet and a bent form that is certainly singlet. E. Bright Wilson *Harvard* reviewed the characteristics of microwave spectroscopy and then discussed a number of recent investigations of chemical interest. The structures of the *cis* form of N_2F_2 and the *trans* form of HSNO were reported. The structure of O_2F_2 is quite unusual in that the oxygen-oxygen bond length is practically as short as in the O_2 molecule, while the oxygen-fluorine distance is unexpectedly long. Wilson concluded his remarks by speculating on the future accomplishments of microwave spectroscopy. He foresees the determination of the complete structure and chemical identity of a molecule about which no information is known except its complete microwave spectrum. He further suggested that a whole range of techniques more or less analogous to those of radiochemistry for handling trace amounts of material could be developed, using microwave spectroscopy as a tool.

It is impossible to give a summary of the entire proceedings of a conference at which 250 papers are presented; the contributions that are referred to here are necessarily those of interest to this reporter. Lionel Salem *Harvard* presented an analysis of the potential constants of diatomic molecules by application of the Hellmann-Feynman theorem. This approach allows estimates to be made of the force constants and anharmonic cubic constants using approximate electron densities and also yields a relationship between the force constant and the quadrupole-coupling constant of either nucleus. R. S. Mulliken *Chicago* gave an extensive discussion of molecular Rydberg states in both homonuclear and heteronuclear diatomic molecules. Laurie and Herschback *Berkeley* considered the isotopic dependence of the zero-point effects and their influence on structural determinations. They showed that, although these isotopic changes in the actual parameters are slight, they can lead to much larger errors in the calculated parameters, as the usual methods of structural analysis magnify the effect of isotopic variations. Oka and Morino *Tokyo* investigated the agreement between the calculated and observed values of the inertia defect ($\Delta = I_{cc} - I_{aa} - I_{bb}$) and found that this agreement is the best criterion for the planarity of a molecule. Morino and his colleagues also discussed an extensive series of investigations of the microwave spectra of molecules in excited vibrational states. By using double Stark modulation and slow mechanical driving of the klystron, they were able to achieve a sensitivity of 2×10^{-9}. This spectrograph coupled with a cell that could be heated to 250°C enabled them to record rotational transitions of molecules in states with as high as five quanta of vibrational energy. These measurements permitted the harmonic and anharmonic potential constants to be determined for OCSe and SO_2, and the assignment of normal vibrations in trioxane $(CH_2O)_3$. Snyder and Schachtschneider *Shell Development* reported on their elegant vibrational analysis of the extended *n*-paraffins from C_3H_8 through *n*-$C_{10}H_{22}$. Using a set of 36 valence force constants to calculate 270 frequencies of these molecules, they were able to obtain a fit to an average error of 0.25% of the values observed at −196°C.

No report of a meeting in Japan would be complete without a comment about the great hospitality this country shows toward visitors. The countryside is as beautiful as it looks in the picture books; the people are as charming as it says in the story books; and the science is as good as it reads in the journals.

Tenth Annual Meeting, Western Spectroscopy Association, Asilomar, California, 24–25 January 1963

Reported by J. C. Decius, Oregon State University

The tenth annual meeting of the Western Spectroscopy Association convened in Asilomar, California, 24 and 25 January 1963, and the eight invited speakers discussed a wide range of spectroscopic subjects. The program was organized in four sessions, entitled "Energy Transfer in Laser Materials", "Solid State", "High Resolution", and "Out of This World", at which M. W. Windsor, K. A. Wickersheim, W. J. Lehmann, and R. A. Satten presided; Satten acted as the general chairman for the meeting.

G. A. Crosby *University of New Mexico* opened the first session with a paper entitled "Energy Transfer in Organic Rare-Earth Chelates". Irradiation at 3500 Å excites the organic part, D = trisdibenzoylmethide or B = trisbenzoylacetonate in MB_3 or MD_3, where M is a trivalent rare-earth ion. The work of Dieke provides a wealth of information on the energy levels of the rare earths, and it is possible to compare energy levels of the singlet or triplet systems of the organic part of the complex with the levels of the rare earth. Thus the $^1G_4$ level of Tm^{+3} lies above the triplet level of TmD_3 but below the triplet level of TmB_3.

continued on page 698

The Atomic Spectra of the Rare Earths: Their Presence in the Sun

Charlotte E. Moore

A summary of the present state of analysis of the first and second spectra of the rare-earth elements is presented with an extensive bibliography. The astrophysical importance of these spectra is stressed. Counts are given of the number of lines of each rare-earth spectrum identified at present in the accessible solar spectrum. Most of them appear only in the singly ionized state; exceptions are Eu I, Tm II?, and Yb I. The possible presence of the strongest laboratory line of Ce III in the solar spectrum is suggested. If correct, this is the first evidence of a third spectrum line in the accessible range of the solar spectrum ($\lambda > 3000$ Å).

I. Introduction

The rare earths comprise two interesting groups of chemical elements characterized by the presence of *f*-electrons in the configurations giving rise to their optical spectra. The lanthanides (type 4*f* in the Periodic Chart of the atoms) are the elements of atomic number 58 through 71, Ce through Lu. Although lanthanum, the preceding element ($Z = 57$) has some rare-earth characteristics, it is not included as a "rare-earth" element in the Periodic Table. The actinides (type 5*f*) form the second group; the elements of atomic number 90 through 103, Th through Lw. All having atomic numbers exceeding 92 have been produced artificially. They are highly radioactive and many have short half-lives, a factor that adds to the difficulty of observing their atomic spectra.

The rapid developments in space technology today place an increasing responsibility on the laboratory spectroscopist to provide information about the rare earths. Much of this can be obtained only by thorough and intensive study of the optical spectra of these elements. Special interest centers in the configurations responsible for the ground states of spectra in different degrees of ionization. As the *f*-shell of electrons fills, the similarity in the binding energies of *d*- and *f*-electrons introduces complexities. Frequently, two overlapping configurations produce low terms, and careful observations are required to determine the ground state. Configuration interaction occurs, and various coupling schemes are required to interpret the spectra. Racah[1] has made a detailed study of the theory involved in the general picture, and is continuing theoretical studies of individual spectra. The author has recently prepared a general summary and bibliography of current work on these spectra.[2]

The more highly ionized spectra of rare earths, chiefly fourth spectra, have been observed in crystals. These observations reveal the low levels of the respective ions as well as the structure due to the crystal field. Optical spectra are required, however, to determine the atomic energy levels and configuration structure giving rise to the complex array of terms that characterize rare-earth spectra.

Progress with analysis is seriously hampered today by the lack of complete and homogeneous line lists of the spectra of each element, with the lines of the various spectra of different stages of ionization clearly and accurately separated. By the use of the hollow cathode, the electrodeless lamp, the dc arc, the sliding spark, and the ring discharge as sources, it is now possible to separate the spectra clearly. Special techniques suitable for producing self-reversed lines are useful guides for detecting the "*raies ultimes*" and other lines arising from the low terms.[3]

Another invaluable tool for the interpretation is the Zeeman effect, which shows the splitting of the lines into characteristic Zeeman patterns when the spectrum is observed in a magnetic field. Resolved Zeeman patterns reveal the *g* values (magnetic splitting factors) and the *J* values (inner quantum numbers) of the two states involved in the transition giving rise to a particular line. A further refinement is provided by experiments

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Table I. Current Observations of Rare-Earth Spectra (February 1963)[a]

Lanthanides

		Range of observations		Range measured		
Z	Sp	Line spectra	Zeeman effect	Line list	Zeeman effect	Reference
58	Ce II	3300–4400 Å 4800–6180 Å				10
	Ce I	3300–4400 Å 4800–6180 Å	3000–7000 Å	3300–4400 Å 4800–6180 Å	5000–5500 Å 6650–7000 Å	10
59	Pr II } Pr I }	2000–8800 Å	4000–8800 Å	2000–8800 Å	4000–5000 Å	11
60	Nd II } Nd I }	2400–9200 Å		3231–8656 Å } 3358–8744 Å }		12
61	Pm	2800–5600 Å				13
	Pm II } Pm I }	3550–8498 Å				14
69	Tm II	2162–11700 Å	2500–8800 Å	4360–11700 Å	2477–6436 Å	6, 15, 52
	Tm I	2500–11700 Å	2800–8800 Å	3300–11700 Å	3000–8800 Å	6, 15, 52
70	Yb	10267–24552 Å		10267–24552 Å		56
	Yb II	2018–24377 Å	2186–8782 Å	2018–24377 Å	2186–8782 Å	15, 52
	Yb I	2240–24552 Å	2464–8325 A	2290–24552 Å	2672–8325 Å	15, 52
71	Lu II	2100–11338 Å		2100–11338 Å		16
	Lu I	8578–24612 Å		8578–24612 Å		17

Actinides

		Range of observations		Range measured		
Z	Sp	Line spectra	Zeeman effect	Line list	Zeeman effect	Reference
90	Th II	2012–10942 Å		2012–10942 Å		18
	Th I	2028–11558 Å	3200–9800 Å 6300–8600 Å	2028–11558 A	3200–9800 Å	11, 18
92	U	8692–23157 Å 3439–5500 Å		8692–23157 Å 3439–5500 Å		19 20
93	Np	8943–22369 Å		8943–22369 Å		21
94	Pu II		2900–4800 Å		2900–4800 Å	22
	Pu	2426–24964 Å		2426–24964 Å		23
	Pu I		3232–6535 Å		3232–6535 Å	24

[a] Supplement to report in J. Opt. Soc. Am. **50**, 407 (1960) (ref. 9).

with the atomic-beam magnetic-resonance technique. This method provides observed g and J values for the components of the lowest terms.

One characteristic of complex rare-earth spectra is that the connection between sets of terms from overlapping configurations can be worked out only from observations in the red and infrared regions. This fact was noted especially by Laporte[4] and was brilliantly illustrated by Racah[5] when he discovered the connection between the two independent groups of terms in Ce II reported by Albertson, thus proving that the ground state was in Group II.

Productive research on the analyses of rare-earth spectra is well begun, but a rich future lies ahead for the spectroscopists working in this field.

II. Laboratory Spectra

A general discussion of the third and fourth spectra of the lanthanides is being presented in this issue by G. H. Dieke. Comments on two of these spectra, may, however, be in order. At the National Bureau of Standards, Sugar[6] has observed and measured Ce III from 840 Å to 11000 Å, preparatory to extending the early analysis of this spectrum in 1937 by Russell *et al.*[7]

A monograph has been prepared by Sugar[8] on Pr III, and this work is being continued. Some 1700 lines have been classified among 118 odd and 130 even levels of the configurations $4f^3$; $4f^2 5,6d$; $4f^2 6p$; $4f^2 6s$; and $4f\ 5d^2$. The ground state is $4f^3\ {}^4I^\circ_{4^1/_2}$. An ionization potential of 23.2 eV has been derived from the two-member *nd* series. The observations extend from 2025 to 10716 Å.

A brief summary of our knowledge of rare-earth spectra was prepared by the author in 1958.[9] A current extension to this summary is presented in Table I for first and second spectra. Only more recent observations are mentioned here. For the individual spectra, successive columns list the range covered by the new *observations*, with line spectra and Zeeman observations handled in separate columns. Then follows similar information for the spectral range *measured* to date, in the two classes of observations. In the

Table II. Summary of Analysis—Lanthanides (February 1963)

Z	Sp	Ground state	Observed configurations	I.P.	Reference
58	Ce II	$4f\ \ 5d^2\ \ {}^4H^\circ_{3^1/_2}$	$4f\ \ 5d\ nx$ $nx = 6s, 6p$		5, 25, 26
			$4f\ \ 6s\ 6p$		
			$4f^2\ \ nx$ $nx = 5d, 6s, 6p$		
			$5d^2\ \ nx$ $nx = 4f, 6s$		
			$5d\ \ 6s^2$		
			$4f^3$		
			$5d^3$		
	Ce I	$4f\ \ 5d\ \ 6s^2\ {}^1G^\circ_4$	$4f\ \ 5d\ 6s^2$	[5.60]	10, 27, 28
			$4f\ \ 5d^2\ 6s$		
			$4f\ \ 5d\ 6s\ \ 6p$		
59	Pr II	$4f^3\ \ 6s\ \ {}^5I^\circ_4$	$4f^3\ \ nx$ $nx = 5d, 6s, 6p$		11, 29, 33
	Pr I	$4f^3\ \ 6s^2\ {}^4I^\circ_{4^1/_2}$	$4f^3\ \ 6s^2$	[5.48]	11, 30–33
60	Nd II	$4f^4\ \ 6s\ {}^6I_{3^1/_2}$	$4f^3\ \ 5d\ 6s$		12, 34
			$4f^4\ \ nx$ $nx = 5d, 6s, 6p$		
	Nd I	$4f^4\ \ 6s^2\ {}^5I_4$	$4f^3\ \ 5d\ 6s^2$	[5.51]	12, 27, 31, 35
			$4f^4\ \ 6p\ \ \ nx$ $nx = 5d, 6s$		
			$4f^4\ \ 6s^2$		
61	Pm I	$4f^5\ \ 6s^2\ {}^6H^\circ_{2^1/_2}$	$4f^5\ \ 6s^2$		14, 30, 36
62	Sm II	$4f^6\ \ 6s\ \ {}^8F_{0^1/_2}$	$4f^6\ \ nx$ $nx = 5d, 6s, 6p$	11.4	37
	Sm I	$4f^6\ \ 6s^2\ {}^7F_0$	$4f^5\ \ 5d\ 6s^2$	5.6	27, 38–40
			$4f^6\ \ 6s\ \ \ nx$ $nx = 6p, 7s$		
			$4f^6\ \ 6s^2$		

continued

Z	Sp	Ground state	Observed configurations	I.P.	Reference
63	Eu II	$4f^7$ $6s$ $^9S°_4$	$4f^6$ $5d$ nx nx = 6s, 6p	11.24	41
			$4f^6$ $5d^2$		
			$4f^7$ nx		
			nx = 6, 7, 8s; 6p; 5, 6d		
			$4f^8$		
	Eu I	$4f^7$ $6s^2$ $^8S°_{3½}$	$4f^7$ $6s$ nx nx = 7, 8s; 6, 7p; 5, 6, 7d; 5, 6f	5.67	40, 42, 43
			$4f^7$ $5d$ $6p$		
			$4f^7$ nx^2 nx^2 = $5d^2$, $6s^2$, $6p^2$		
64	Gd II	$4f^7$ $5d$ $6s$ $^{10}D°_{2½}$	$4f^7$ $5d$ nx nx = 6s, 6p		44
			$4f^7$ nx^2 nx^2 = $5d^2$, $6s^2$		
	Gd I	$4f^7$ $5d$ $6s^2$ $^9D°_2$	$4f^7$ $5d$ $6s$ nx nx = 6p, 7s	6.16	27, 44
			$4f^7$ $5d^2$ nx nx = 6s, 6p		
			$4f^7$ $6s^2$ nx nx = 5d, 6p, 7s		
65	Tb I	$4f^9$ $6s^2$ $^6H°_{7½}$	$4f^9$ $6s^2$	[5.98]	3, 28, 30
66	Dy II	$4f^{10}$ $6s$ $^6I_{8½}$	$4f^{10}$ $6s$		45, 46
	Dy I	$4f^{10}$ $6s^2$ $^5I_8$	$4f^{10}$ $6s^2$		27, 36, 47
67	Ho I	$4f^{11}$ $6s^2$ $^4I°_{7½}$	$4f^{11}$ $6s^2$		36, 48
68	Er II	$4f^{12}$ $6s$ $^4H_{6½}$	$4f^{11}$ $6s$ $6p$		49–51
			$4f^{11}$ nx^2 nx^2 = $5d^2$ $6s^2$		
			$4f^{12}$ nx nx = 6s, 6p		
	Er I	$4f^{12}$ $6s^2$ $^3H_6$	$4f^{12}$ $6s^2$	[6.08]	27, 28, 36

continued

Z	Sp	Ground state	Observed configurations	I.P.	Reference
			$4f^{12}\ 6s\ nx$ $nx = 5d, 6p$		6, 15, 52
69	Tm II	$4f^{13}\ 6s\ {}^2F^\circ_4$	$4f^{12}\ 6s^2$		
			$4f^{13}\ nx$ $nx = 5d, 6s$		
			$4f^{13}\ 6s\ nx$ $nx = 6p, 7s, 8s$	5.81 ± 0.02	6, 15, 52, 53
	Tm I	$4f^{13}\ 6s^2\ {}^2F^\circ_{7/2}$	$4f^{13}\ 5d\ 6p$		
			$4f^{13}\ 6s^2$		
			$4f^{13}\ 6s\ nx$ $nx = 5d, 6p$	12.05	15, 46, 52, 55
70	Yb II	$4f^{14}\ 6s\ {}^2S_{0^1/_2}$	$4f^{13}\ 5d\ 6p$		
			$4f^{13}\ nx^2$ $nx^2 = 5d^2, 6s^2$		
			$4f^{14}\ nx$ $nx = 5d;\ 6p;\ 6, 7s$		
			$4f^{14}\ 6s\ nx$ $nx = 5, 6d;\ 6p;\ 7, 8s$	6.22	15, 52, 54, 55
	Yb I	$4f^{14}\ 6s^2\ {}^1S_0$	$4f^{13}\ 5d\ 6s^2$		
			$4f^{14}\ 6s\ nx$ $nx = 5, 6d;\ 6p;\ 7s$	14	16, 57
71	Lu II	$4f^{14}\ 6s^2\ {}^1S_0$	$4f^{14}\ 5d\ nx$ $nx = 6p, 7s$		
			$4f^{14}\ nx^2$ $nx = 5d^2\ 6s^2$		
			$4f^{14}\ 5d\ 6s\ nx$ $nx = 6p, 7s$	6.15	17, 57, 58
	Lu I	$4f^{14}\ 5d\ 6s^2\ {}^2D_{1^1/_2}$	$4f^{14}\ 6s^2\ nx$ $nx = 5, 6d;\ 6, 7p;\ 7s$		
			$4f^{14}\ 6s\ nx^2$ $nx^2 = 5d^2, 6p^2?$		

Table III. Summary of Analysis—Actinides (February 1963)

Z	Sp	Ground state	Observed configurations	I.P.	Reference
90	Th II	$6d^2\ 7s\ {}^4F_{1/2}$	$5f\quad 6d\ nx$ $nx = 7s, 7p$		59, 60
			$5f\quad 7s\ 7p$		
			$5f\quad nx^2$ $nx^2 = 6d^2, 7s^2$		
			$5f^2\quad nx$ $nx = 6d, 7s, 7p$		
			$6d\quad 7s\ 7p$		
			$6d\quad 7s^2$		
			$6d^2\quad nx$ $nx = 7s, 7p$		
			$6d^3$		
	Th I	$6d^2\ 7s^2\ {}^3F_2$	$6d\quad 7s^2\ 7p?$	[6.95]	11, 18, 28, 59–63
			$6d^2\quad 7s\ 7p?$		
			$6d^2\quad 7s^2$		
			$6d^3\quad nx$ $nx = 7s, 7p?$		
91	Pa I	$5f^2\ 6d\ 7s^2\ {}^4K_{5/2}$	$5f^2\quad 6d\ 7s^2$		64, 92
92	U II	$5f^3\quad 7s^2\ {}^4I^\circ_{9/2}$	$5f^3\quad 7s\ nx$ $nx = 6d, 7p$		3, 65–70
			$5f^3\quad nx^2$ $nx^2 = 6d^2, 7s^2$		
			$5f^1\quad nx$ $nx = 6d, 7s, 7p$		
	U I	$5f^3\quad 6d\ 7s^2\ {}^5L^\circ_6$	$5f^3\quad 6d\ 7s^2$	[6.08]	19, 20, 28, 64 68, 69, 71–73
			$5f^3\quad 6d^2\ 7s$		
93	Np I	$5f^4\quad 6d\ 7s^2\ {}^6L_{11/2}$	$5f^4\quad 6d\ 7s^2$		64, 74, 93
94	Pu II	$5f^6\quad 7s\ {}^8F_{0^1/2}$	$5f^6\quad 7s$		22
	Pu I	$5f^6\quad 7s^2\ {}^7F_0$	$5f^6\quad 7s^2$		24, 75–78
95	Am II	$5f^7\quad 7s\ {}^9S^\circ_4$	$5f^6\quad 6d\ 7s$		79
			$5f^7\quad nx$ $nx = 6d, 7s$		
	Am I	$5f^7\quad 7s^2\ {}^8S^\circ_{7/2}$	$5f^6\quad 6d\ 7s^2$	6.0	79–82
			$5f^7\quad 7s\ nx$ $nx = 6, 7d;\ 7p, 8s$		
			$5f^7\quad 7s^2$		
96	Cm I	$5f^7\quad 6d\ 7s^2\ {}^9D^\circ_2$	$5f^7\quad 6d\ 7s^2$		64, 83

last column, the numbers refer to the references at the end of this paper.

Table II summarizes the present work on the analysis of first and second spectra of the lanthanide group. The various entries are self-explanatory. The ionization potentials in column 5 are entered in brackets for the spectra in which series have not yet been observed in the optical spectra. The bracketed entries are experimental values determined by a "surface ionization method" in which the ionization potentials relative to those from well-known series have been observed. The method is described in the individual papers for which the reference is given in column 6. The extensive list of references following the paper gives the source material used for the various spectra. Table III, arranged similarly, gives the same information for the first and second spectra in the actinide group.

Volume IV of "Atomic Energy Levels" will deal exclusively with rare-earth spectra. At present the data are too incomplete for the preparation of this manuscript, but it is hoped that the programs in various laboratories will progress sufficiently to make this volume a reality in the foreseeable future.

This publication will start with Ce I, a complex spectrum that has been so incompletely observed that it has defied analysis through the years, until fairly recently. From a study of strong lines observed in absorption and from Zeeman-effect observations the analysis has now been started by Martin in this laboratory.[10] He points out that the principal Russell-Saunders component for the ground state is $^1G^\circ_4$ (g = 0.945), but that the coupling is intermediate in the configuration of this state, $4f\,5d\,6s^2$. Three g values previously determined for Ce I by atomic beam methods[27] agree satisfactorily with those from the optical Zeeman effect not only for this $^1G^\circ_4$ term, but also for the low levels of a $^3F^\circ$ term (J = 2, 3) from the same configuration. In addition to a number of other low "odd" levels Martin has also found about 120 "even" levels to date.

Ce I is cited as an illustration of the urgent need for more extensive and careful work on the analyses of these incompletely known spectra urgently needed to conclude the writer's program on "Atomic Energy Levels."

III. Astrophysical Aspects

Astronomers have long recognized the astrophysical importance of the rare earths. Merrill[84] has given a history of these spectra and of their occurrence in stellar spectra of various types. Europium is of special interest. Lines of Eu II are abnormally strong in some peculiar A-type stars. "Marked variations of line intensities in periods of a few days are characteristic of these stars. A remarkable circumstance is that changes in lines of certain elements may occur with phases differing from those of lines of other elements by as much as half a period." The most conspicuous example is the star α^2 Can Ven, a star having a general magnetic field varying in the same period in which the line intensities vary, according to Babcock and Burd.[85] "Lines of Eu II are abnormally strong. . . in many other magnetic stars." A comprehensive discussion of the magnetic stars may be found in a paper published by Babcock in 1958.[86]

In the more general studies of stellar evolution, the theoretical investigators have suggested that rare earths may provide one of the necessary links in the development of atomic syntheses.[87]

More and more stellar spectra are being observed with high-dispersion instruments. Hundreds of stellar lines in spectra of various types remain unidentified. It is safe to predict that rare-earth spectra may play a very important role in the further interpretation of these spectra, when sufficient laboratory data on the individual spectra become available. Even with the present limited material, it may be pertinent to describe the identification of rare earths in the solar spectrum as an illustration of one astrophysical aspect in applied optics.

Table IV contains the summary of the rare-earth lines identified in the second revision of Rowland's Solar Spectrum Table, which is now in course of preparation.[88] The range covered in this work is 2935 to 8770 Å. Under each spectrum the number of lines in each of three groups is tabulated. The three groups have the following meanings:

Present—The rare-earth line is present and unblended in the solar spectrum, i.e., it accounts entirely for the observed intensity of the solar line. Lines identified as present with a question, though unblended, are included in these counts.

Blend—The rare-earth line is present but is only a partial contributor to the observed solar line.

Masked—The rare-earth line is masked in the solar spectrum. Only strong laboratory lines are counted here and entered in the solar table as masked. Many fainter ones are also masked, but not included in the count.

Because of the comparatively low-ionization potentials, there are very few spectra of neutral rare-earths represented in the sun. The sun-spot spectrum is a more favorable source for these, but even here only two first-spectra are definitely known, namely Eu I and Yb I. In both of these spectra the intensity is more concentrated in a few very strong lines, than is the case for other elements.

Eu I is of special interest. In multiplet (1) the "*raie ultime*" is masked by a strong solar line. The other two lines in the multiplet were detected in the spot spectrum. One appears faintly in the disk spectrum, and the other is present only in the spot spectrum. Less dissociation occurs in the spot spectrum, and, con-

Table IV. Rare Earths in the Solar Spectrum

Z	Sp	Number of lines				Sun		
		Present	Blend	Masked	Total	Maximum disk int. ($\Delta\lambda/\lambda$)	Spot behavior	Wavelength (Å)
58	Ce III?	1	—	—	1	trace	—	3055.594
	Ce II	105	61	20	186	13.7	—	3560.802
59	Pr II	13	7	1	21	3.9	—	3994.810
60	Nd II	68	34	4	106	15.1	s	4303.595
62	Sm II	88	47	11	146	18.0	—	3735.964
63	Eu I	2	0	1	3	0.9	s	4627.221
	Eu II	12	5	3	20	28.2	—	3819.688[a]
64	Gd II	39	24	11	74	26.4	—	3439.805
65	Tb II?	4?	1?	8?	13?	1.8	—	3568.55
66	Dy II	39	17	5	61	18.8	—	3407.805
67	Ho II	Insufficient laboratory data						
68	Er II	1	0	1	2	8.7	u	3896.248
69	Tm I	2?	—	—	2?	0.9	—	4094.20
	Tm II	6	4	—	10	5.1	—	3172.852
70	Yb I	1	1	—	2	5.0	s	3987.966[a]
	Yb II	1	1	—	2	25.6	s	3694.199[a]
71	Lu II	1	2	—	3	12.1	—	3397.062
90	Th II	1	—	—	1	2.1	—	4019.136[a]

[a] *Raie ultime.*

sequently, this is a more favorable source for neutral lines of rare earths, as is beautifully illustrated by Eu I.

The strongest Tm I line does not appear to be present in the spot spectrum, which makes its presence in the disk spectrum dubious, as indicated by the question mark.

In the spectrum of the solar chromosphere the lines of the second spectra are well known. Menzel[89] noted the characteristic behavior of these lines in that they do not reverse in going from the emission spectrum of the solar chromosphere to the absorption spectrum of the disk, but rather they appear in emission far in on the solar disk, unlike lines in the spectra of other elements. This has been further confirmed by Thackeray.[90]

The presence of Tb II in the sun is doubtful, but it is included here because of its possible presence in the chromospheric spectrum, where the characteristic described above has been noted for some of the lines. Similar evidence adds confirmation to the identification of Er II in the disk spectrum.

Special mention should be made of Ce III. The strongest observed line is one at 3055.589 Å, which agrees well with a very faint solar line at 3055.594 Å, first recorded by Rowland and not otherwise identified. This line is not the "*raie ultime*" of Ce III, but it was classified by Russell *et al.*[7] as the leading member of multiplet (1). Sugar has since confirmed the relative intensity, from recent observations.[6] The solar identification is entered with a question pending further analysis based on more complete laboratory observations. This is the first suggestion of a third spectrum line in the accessible solar spectrum. It does not appear unreasonable in view of the low ionization potential of Ce I (5.6 eV ±), the presence of Ce II lines in the sun, and the strength of this Ce III line in the laboratory spectrum.

The last three columns of Table IV contain solar data. Column 7 gives the maximum observed solar intensity of a clearly unblended line in each rare-earth spectrum detected in the sun. For each spectrum the reduced equivalent width of the line ($\Delta\lambda/\lambda$) as recorded by Minnaert and his staff[91] is tabulated. In the column headed "spot" the behavior of the line in the spot spectrum is indicated by two letters: s, meaning strengthened in intensity as compared to the disk spectrum; u, unchanged in intensity in the spot. No spot intensities are available for wavelengths short of 3894 Å.

The last column gives the solar wavelength of the rare-earth line having the maximum solar intensity in column 7.

To date only one line in the spectrum of an actinide element has been detected in the solar spectrum. This is the "*raie ultime*" of Th II.

When Volume IV of "Atomic Energy Levels" has been completed, Multiplet Tables can be prepared for the astrophysicist that will greatly extend our knowledge of rare earths in the stars. Table IV should be extended to cover the range of the solar spectrum from the x-ray to the microwave region. The study of rare

earths in other stellar spectra over the same range should be a most rewarding astrophysical project in applied optics of the future.

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Meetings Calendar

July

1–5 IUPAC Internatl. Symp. on Macromolecular Chem., Paris *Symp. Sec., Lab. de Chimie Physique, 11, rue Pierre Curie, Paris 5, France*

1–5 Gordon Conf. on Chemistry and Physics of Space, Tilton School, Tilton, N.H.

1–14 Applications of Quantum Mechanical Methods to the Study of Molecular Properties, Menton *R. Daudel, Centre de Mechanique Ondulatoire Appliquee, 23, rue du Maroc, Paris 19, France*

2–5 Internatl. Symp. on Free Radicals, 6th, Cambridge *A. B. Collear, U. of Cambridge, Lensfield Rd., Cambridge, England*

5–9 IUPAC Conf., London *Sec., IUPAC Conf., 47 Belgrave Sq., London, SW1, England*

8–13 Ionization Phenomena in Gases, Orsay *P. Hubert, CENFAR, B. P. No. 6, Fontenay-aux-Roses, Seine, France*

8–19 Industrial Use of the Polarizing Microscope, McCrone Res. Inst. *J. A. Reffner, McCrone Res. Inst., 451 E. 31 St., Chicago 16, Ill.*

8–27 Summer Course in Modern Optics, Inst. of Optics, U. of Rochester *Inst. of Optics Summer Course, U. of Rochester, River Campus Station, Rochester 20, N. Y.*

10–17 IUPAC Congress, London *Sec., IUPAC Congress, 47 Belgrave Sq., London, SW1, England*

15–19 IUPAP, 2nd Internatl. Conf. of Nuclidic Masses, Vienna, Austria

15–19 Fundamentals of Infrared Technology summer course, U. of Mich. *Engr. Summer Confs., W. Engr. Bldg., U. of Mich., Ann Arbor, Mich.*

15–26 Optical Physics and Its Applications Course, UCLA *Engr. Ext., Engr. Bldg. U. of Calif., Los Angeles 24, Calif.*

18–20 Conf. on Vibrational Spectroscopy of Macropolymers, Milan *G. Zerbi, Inst. de Chimia Industrial del Polytechnico, Piazza Leonardo da Vinci 32, Milan, Italy*

18–23 IUPAC Symp. on Thermodynamics and Thermochemistry, Lund *S. Sunner, Thermochem. Lab., Lund U., Lund, Sweden*

22–26 Physics of Electronic and Atomic Collisions, London *Conf. Sec., Physics Dept., University Col., Gower St., London, WC 1, England*

22–26 Symp. on Microscopy, Brighton, England *E. C. Bitoy, McCrone Res. Inst., 451 E. 31 St., Chicago 16, Ill.*

22–27 European Molecular Spectroscopy Mtg., Budapest *A. Kovacz, Hungarian Academy of Sciences, Budapest, Hungary*

24–Aug. 9 The Microscope in Criminalistics, McCrone Res. Inst. *J. A. Reffner, McCrone Res. Inst., 451 E. 31 St., Chicago 16, Ill.*

30–Aug. 9 U. of Minn. Molecular Spec. Lab Summer Courses in IR Spectroscopy *Director, Center for Continuation Study, U. of Minn., Minneapolis 14, Minn.*

August

4–9 Internatl. Conf. and Exhibit on Aerospace Support, Wash., D.C. *Box 6635, Wash., D.C.*

5–9 Optical Masers—Theory, Technology, and Applications, summer course, U. of Mich. *Engr. Summer Confs., W. Engr. Bldg., U. of Mich., Ann Arbor, Mich.*

5–9 Soc. of Photographic Instrumentation Engrs., Ambassador Hotel, Los Angeles *J. A. Clemente, Pacific Missile Range, Pt. Mugu, Calif.*

5–16 Radiation Thermometry Course, UCLA *Engr. Ext., Engr. Bldg., U. of Calif., Los Angeles 24, Calif.*

12–16 Fundamentals of Infrared Technology, summer course, U. of Mich. *Engr. Summer Confs., W. Engr. Bldg., U. of Mich., Ann Arbor, Mich.*

12–16 Gordon Conf. on Instrumentation, Colby Jr. Col., New London, N.H.

12–16 Gordon Conf. on Chemistry and Physics of Solids, Kimball Union Acad., Meriden, N.H.

13–17 5th Ann. Gas Chromatography Session, Fisk U. *N. Fuson, Fisk Infrared Inst., Fisk U., Nashville 8, Tenn.*

13–23 14th Ann. Infrared Spectroscopy Inst., Fisk U. *N. Fuson, Fisk Infrared Inst., Fisk U., Nashville 8, Tenn.*

15–30 Internatl. Assoc. of Meteorology and Atmospheric Physics, Berkeley, Calif. *W. L. Godson, Meteorological Office, 315 Bloor St. W., Toronto 5, Ont., Canada*

19–23 Special Topics in Optics, summer course, U. of Mich. *Engr. Summer Confs., W. Engr. Bldg., U. of Mich., Ann Arbor, Mich.*

19–23 Infrared Spectroscopy Inst., Canisius Col. *H. A. Szymanski, Canisius Col., Buffalo 8, N.Y.*

19–29 Summer Seminar on Pictorial Data Processing and Pattern Recognition, Yeshiva U., NYC *A. Rosenfeld, Belfer Grad. School of Science, Yeshiva U., New York 33, N.Y.*

19–30 Thermal and Luminous Radiative Transfer Course, UCLA *Engr. Ext., Engr. Bldg., U. of Calif., Los Angeles 24, Calif.*

19–30 Advanced Crystallography, McCrone Res. Inst. *J. A. Reffner, McCrone Res. Inst., 451 E. 31 St., Chicago 16, Ill.*

20–23 Australian Spectroscopy Conf., Canberra *E. Spinner, Australian Natl. U., Canberra, Australia*

26–30 Masers-Lasers Course, UCLA *Engr. Ext., Engr. Bldg., U. of Calif., Los Angeles 24, Calif.*

26–30 Gordon Conf. on Glass, Tilton School, Tilton, N.H.

26–30 Internatl. Symp. on the Solar Spectrum, Utrecht *C. de Jager, Theoretical Dept., Sterrewacht, Servaasbolwerk 13, Utrecht, Netherlands*

27–31 Hungarian Soc. of Optics, Acoustics and Film Techniques, Conf. on Scientific and Appl. Photography, Budapest *Optikai, Akusztikai és Filmtechnikai Egyesület, Szabadság tér 17, Budapest V, Hungary*

28–31 APS, Edmonton, Alta., Canada *W. A. Nierenberg, U. of Calif., Berkeley 4, Calif.*

29–30 Solvation Symp., U. of Alberta *P. J. Krueger, Chemistry, U. of Alberta, Calgary, Alba., Canada*

September

— Internatl. Commission on Glass, 14th Ann. Mtg., Lausanne *R. Günther, Bockheimer Landstr. 126, Frankfurt am Main, Germany*

— British Assoc. for the Advancement of Science, 125th Ann. Mtg., Aberdeen, Scotland *G. Allen, Burlington House, London, W. 1, England*

— Internatl. Conf. on Information Theory, Sendai, Japan *G. L. Turin, U. of Calif., Berkeley, Calif.*

The Spectra of the Doubly and Triply Ionized Rare Earths

G. H. Dieke and H. M. Crosswhite

The present status of our knowledge of the structure of the spectra of the doubly and triply ionized spectra of the rare earths is derived partly from experimental data of the emission spectra of the free ions which provide the energy level scheme in great detail but are difficult and laborious to analyze. For the lower levels knowledge of the structure comes from the crystal absorption and fluoresence spectra. In all cases approximate theoretical calculations of the energies are essential.

I. Introduction

The rare earths, in common with the actinides, have the most complicated spectra of any of the elements. This is because the incomplete 4*f*-shell produces a very large number of low-lying levels. The transitions between these give a many-line spectrum without any apparent regularities. Even multiplets, which are such prominent features of the spectra of the transition elements, are in general unrecognizable. For these reasons the rare-earth spectra have long been neglected. Because of the growing importance of the rare earths in recent years, their spectra have received renewed attention. In the present article we shall restrict ourselves to the spectra of the doubly and triply ionized elements for several reasons.

Most atomic spectra are obtained by vaporizing the element, exciting the vapor by an electric discharge, and thus obtaining the emission spectrum of the free ions or neutral atoms. The triply ionized rare earths, and to a lesser extent also the doubly ionized ones, can be incorporated into crystal lattices where they retain their sharp energy levels only slightly modified by the internal crystal field. This makes it possible to obtain some of the energy levels, particularly the important low ones, from the absorption and fluorescence spectra of crystals containing these rare earths.

An extensive program of the study of the spectra of doubly and triply ionized rare earths is under way at Johns Hopkins University and both the emission spectra of the free ions and the crystal spectra are investigated. One of the chief purposes of this study is the comparison of the levels of the free rare-earth ion with those of the same ion in a crystal lattice, in order to be able to obtain an exact evaluation of the influence of the crystal field. The present paper is a report of the work carried out or planned for the immediate future at Johns Hopkins University.

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II. Experimental Techniques

The free-ion spectra are obtained from a controlled spark in a rare-gas atmosphere at reduced pressure.[1] Figure 1 shows the development of the spectrum of gadolinium as the circuit parameters are changed. The 3-A spectrum is that of a dc arc, and even at this low-excitation lines of the doubly ionized ion appear. The other spectra are of unidirectional pulsed discharges, the duration varying from about 2 msec for 100 A to 100 μsec for 1500 A. Above 100 A there is no trace of the second (singly ionized) spectrum, and as the excitation is increased the third also gradually gives way to the fourth. In no case is the spectrum completely pure for a given ionization stage, but by comparing one which contains only third and fourth ("hot spark") with one containing only second and third ("mild spark") the fourth spectrum lines may be identified. The lower excitation of an arc or microwave discharge is also needed to eliminate the first and second spectra, but for our purposes it is not necessary to distinguish between the two. It is important for this separation that the pulsed discharge not be allowed to oscillate as this will superimpose a lower excitation discharge on the high and make the suppression of the second spectrum difficult.

Figure 2 shows a comparison of hot and mild sparks for various wavelength regions of the neodymium spectrum. In the upper section Nd IV lines predominate for the hot spark (A) although some very weak Nd III may be found. A slightly longer wavelength region (center) is very rich in Nd III. Even longer wavelengths (bottom) show mainly II and I in the mild spark (B) and very little in the hot. This separation by wavelength is also very significant for the analysis and is discussed further in Sec. IV.

Accurate wavelength measurements are of the greatest importance as the possibility for finding spurious

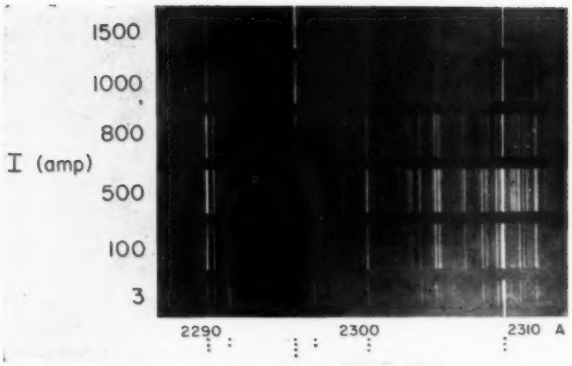

Fig. 1. Stages of ionization. Different excitation conditions in the gadolinium spectrum. Lines of Gd II, III, and IV are indicated by corresponding sets of dots. The 3-A spectrum is that of a dc arc, the others are pulsed, critically damped discharges.

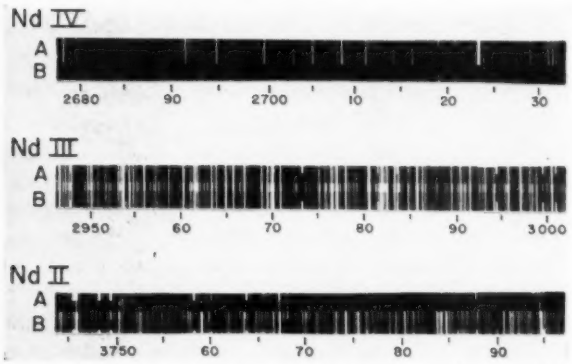

Fig. 2. A—900-A peak current discharge (hot spark); B—50-A peak (mild spark). All spectrum regions were taken simultaneously. The short lines on the edges are from the Fe calibration tube.

regularities is proportional to $(\Delta\nu)^2$, where $\Delta\nu$ is the uncertainty in the frequency measurements. The use of large gratings is therefore most appropriate. In our work a 17.8 cm wide, 6.64 m f.l. concave grating with 1200 lines/mm is used for most of the work, in the first order for the longer wavelengths (above 5000 Å), in the second or third orders for the shorter ones, which makes it possible to obtain wavenumbers accurate to about 0.01 cm^{-1} for most of the spectrum above 2000 Å. The use of an interferometer would not contribute much because, particularly in the hot spark, the lines are not sharp enough for utilizing the greater inherent accuracy of the interferometer. The fact that thousands of lines must be measured in each spectrum makes the use of modern automatic measuring techniques imperative.[2]

For the crystal absorption spectra[3] light from a continuous source, usually a high-pressure mercury or xenon lamp, a tungsten ribbon lamp or a zirconium arc depending on the wavelength region, are passed through a properly oriented crystal immersed in liquid helium. The Zeeman effect is often important, so the dewar vessel must be constructed so that it can fit between the pole pieces of a magnet. At low enough temperature the wavenumbers of the absorption lines directly represent the position of the excited energy levels. The electric crystal field produces a Stark effect which splits all levels into a maximum of $2J + 1$ components for an even number of electrons and $J + {}^1/_2$ components for an odd number. The number and spacing of the components depends on the symmetry and intensity of the crystal field. In most cases the total splitting of a free-ion level is of the order of a few hundred cm^{-1}, in general small compared to the spacing between adjacent multiplet components.

A sharp-line fluorescence spectrum is obtained, containing in some cases several hundred sharp lines,[4] by illuminating the crystal by an intense light source. When the coupling between the electronic level and the crystal lattice is large the excitation energy is dissipated before fluorescence can take place. This is the case for most hydrated salts[5] except for the central rare earths from Sm to Dy. In other lattices all rare earths fluoresce strongly but not from all levels. The anhydrous chlorides and bromides, the garnets and the oxides are among the crystals that show general fluorescence.[6] Figure 3 illustrates this for a crystal of Y_2O_3 containing 1% erbium. From theoretical considerations and previous experience we expect to find a group (called the A group) of excited levels at about 10,000

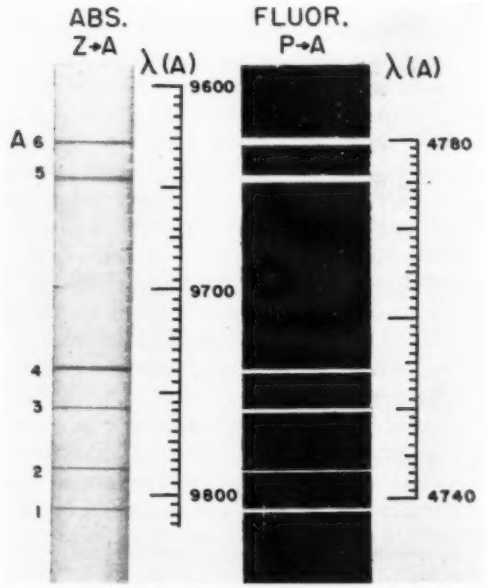

Fig. 3. Absorption and fluorescence spectra of 1 % Er^{3+} in Y_2O_3. Left: Absorption from Z group to A Group ($^4I_{15/2} \rightarrow {}^4I_{11/2}$). Right: Fluorescence from P group to A group ($^2P_{3/2} \rightarrow {}^4I_{11/2}$). See Fig. 7.

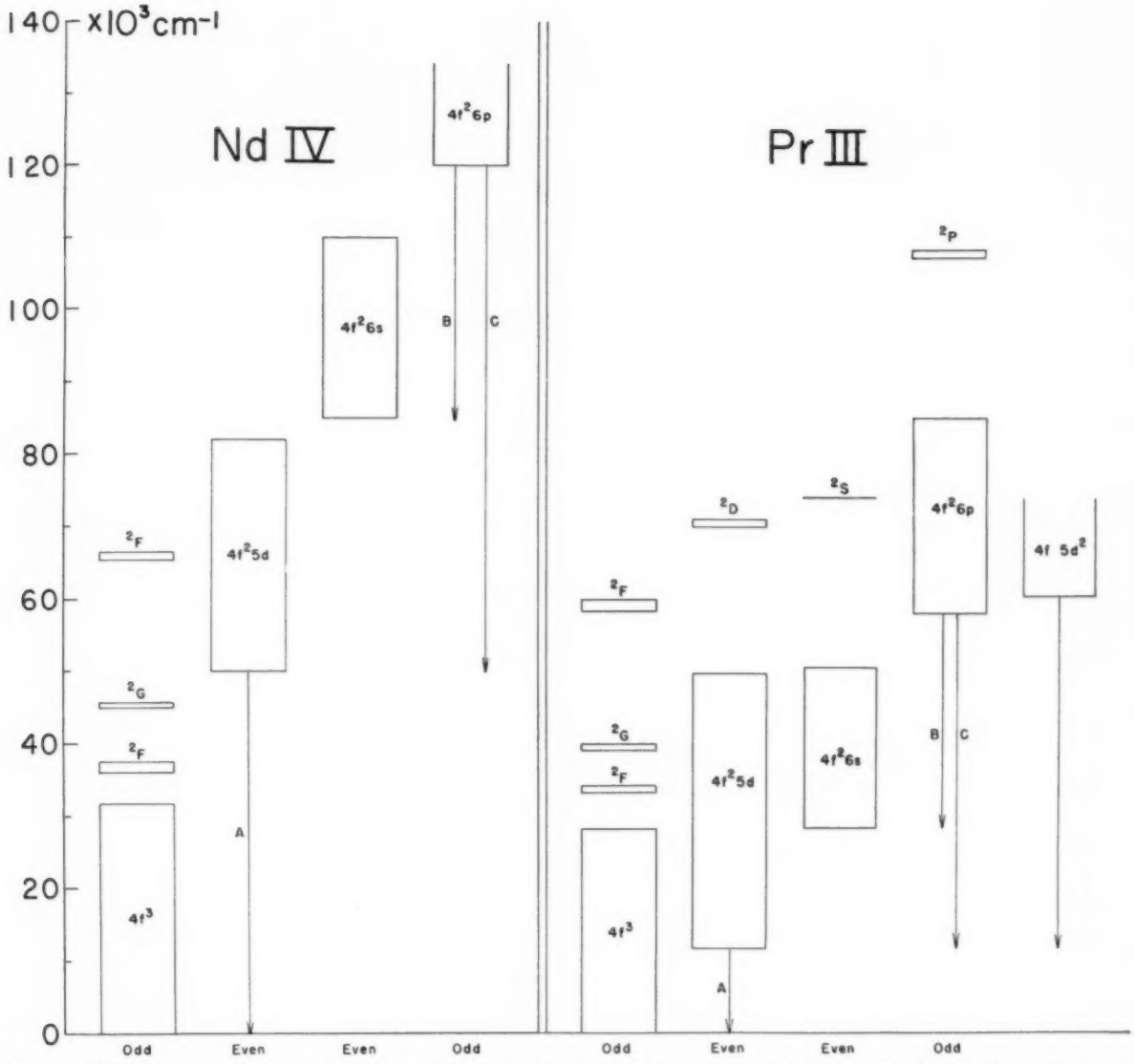

Fig. 4. Block diagram of three-electron configurations Nd IV and Pr III. Arrows indicate principal transitions. Parity is indicated by "odd" or "even."

cm^{-1} above the ground state which would correspond to the single free ion $^4I_{11/2}$ level (see Sec. III, especially Fig. 7). As the number of electrons for Er^{3+} is odd, and as the local crystal field symmetry about this ion is low, we expect to find the Stark-split level to consist of $J + {}^1/_2 = 6$ components. The ground state $^4I_{15/2}$ will be split into 8, but if the crystal is cold enough, only the lowest of these will be occupied. Absorption transitions occur between this lowest level and any higher level unless forbidden by selection rules. All six appear in the left-hand spectrum of Fig. 3. Fluorescence from the lowest Stark component of $^2P_{3/2}$ (P group), shown on the right, confirms all six levels. Very low levels, such as the higher Stark components of the ground state, for which the absorption spectrum is not in an accessible region, must be confirmed by additional fluorescing levels.

In complicated fluorescence spectra, single levels can be excited by monochromatic illumination, and this greatly helps in the analysis of such spectra. The fluorescence spectra are extremely sensitive for very small amounts of impurities, and great care must be taken to identify such impurity lines which occur in even the purest available materials.[7]

For the crystal spectra the task of obtaining the energy level system from the observed wavelengths of the absorption and fluorescence lines is in general direct and simple. For the free-ion emission spectra

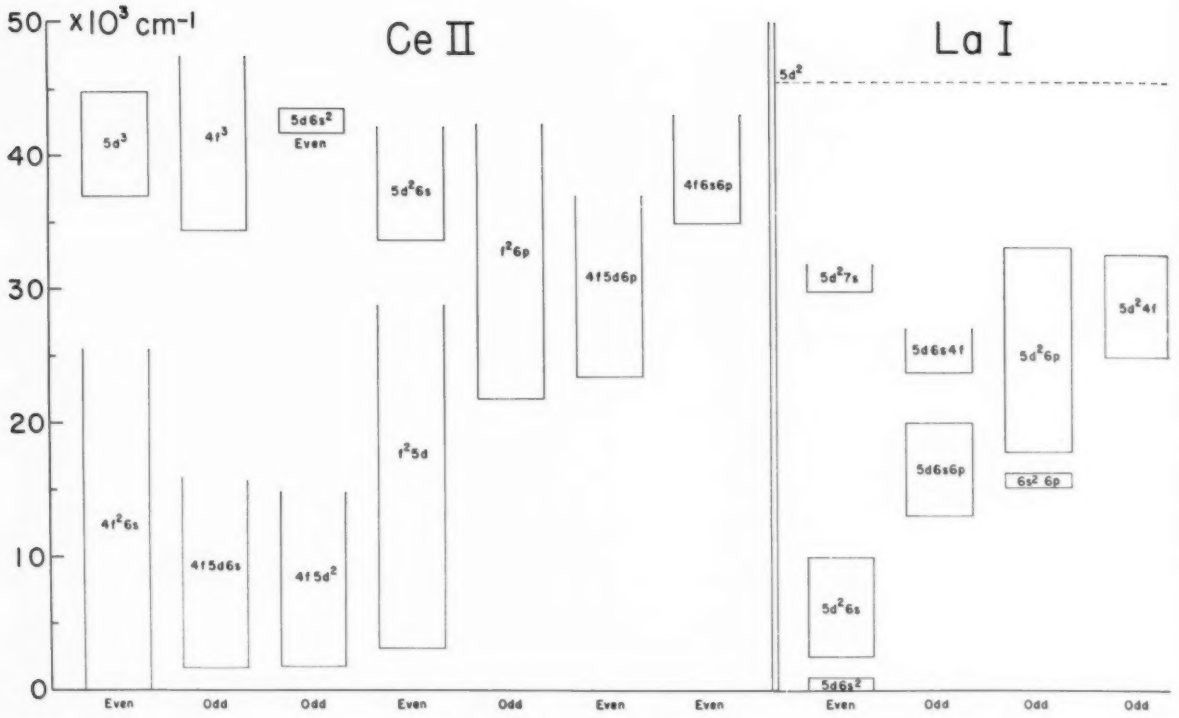

Fig. 5. The same for Ce II and La I.

this is a much more elaborate and difficult problem. It can be solved much more expeditiously when one knows approximately what to expect. In fact, a satisfactory analysis of these complicated spectra would be virtually impossible without a thorough theoretical study of the structure of the energy levels. Such a study is based on the general theory of atomic structure, as for instance set forth in the book by Condon and Shortley[8] or those by Slater,[9] systematized for the complicated rare ion cases by Racah.[10] The specific situation for the rare earths has been clarified by a comparison with the empirical results so far obtained from the crystal and free-ion spectra.

III. Level Structure of the Rare-Earth Ions

It has been known since the early days of the Bohr theory that the $4f$, $5d$, and $6s$ electrons have very nearly the same energy for the rare earths. This is true especially for the neutral and singly ionized atoms. This means that configurations like $4f^n$, $4f^{n-1}5d$, $4f^{n-1}6s$, $4f^{n-2}6s^2$, etc., may overlap and create an extremely complicated set of low-lying energy levels which it is difficult to disentangle. Fortunately, the situation is much clearer for the divalent ions and even more so for the trivalent ones. The reason for this is that because of the higher nuclear charge and the consolidation of the inner shells the screening is more perfect and the levels appear more nearly in the order of their principal quantum numbers. For the fourth spectra the $4f$ orbits always have the lowest energy, then come $5d$, $6s$, and $6p$. This means that without exception the $4f^n$ configuration is lowest, then come $4f^{n-1}5d$, $4f^{n-1}6s$, and $4f^{n-1}6p$, with several other configurations coming in with energies near that of $4f^{n-1}6p$. Figures 4 and 5 show for ions with three external electrons how this situation changes as we go to the lower stages of ionization.

For the third spectra the order of the configurations is still essentially the same as for the fourth, but the beginning of the rare-earth series $4f^n$ and $4f^{n-1}5d$ are nearly coincident and $4f^{n-1}5d$ and $4f^{n-1}6s$ cross over near Dy (see Fig. 6). For the second and first spectra, as Fig. 5 shows, the situation is very confused, and this makes the analysis of these spectra much more complicated than that of the higher ionization stages.

It is, of course, not sufficient to know merely the position of the centers of the configurations as indicated in Fig. 6. We must know their total width and the arrangement of the individual energy levels. The method for doing this can be briefly indicated as follows.

The outer electrons are regarded first to be in a central field provided by the nucleus screened by the 54 electrons of the completed xenon-like shell. For the rare earths the assumption that this central field is a Coulomb field determined by one parameter, the effective nuclear charge Z^*, leads to practically as good

results as the more general assumption of a nonrestricted central field and simplifies the calculations materially. After first considering the outer electrons as completely independent, their electrostatic repulsion and their spin-orbit interactions are introduced by the potentials

$$H^1 = (e^2/r_{ij}) \text{ and } H^2 = \Sigma\zeta_i(s_i l_i)$$

expressing the electrostatic repulsion between the outer electrons and the spin-orbit interaction, and the influence of these perturbing potentials on the energy and wave functions calculated. In performing these calculations interactions between states of only one configuration are taken into consideration, but no further restrictions are made. For the higher stages of ionization, other configurations of the same parity are far away for the lowest configurations and we make no fatal mistake by leaving out interconfiguration interactions, although they are by no means negligible.

The systematics of handling the very large number of individual states have been developed by Racah.[10] It is evident that only states with the same L and S can interact through H^1, only those with the same J through H^2. This and other symmetry considerations greatly limit the number of matrix elements of H^1 and H^2 that have to be calculated and restrict the order of the interaction matrix that has to be diagonalized to the number of different states with the same J occurring in the configuration. The situation is simplest for the $4f^n$ configurations. The calculations, which are somewhat tedious, but not unduly so for a modern computer, are carried out numerically as a function of the spin-orbit parameter ζ and contain a scaling parameter F_2 which is determined by the effective charge Z^*. The two numerical parameters F_2 and ζ are obtained by comparing the calculated set of levels with some well-identified empirical ones.

This has been carried out for all the crystal spectra of the trivalent rare earths, and Fig. 7 gives an example of the agreement that is reached. The 29 lowest of the 41 possible levels of the $4f^{11}$ configuration of Er^{3+} are shown.[12] It is clear that for the first few multiplets there cannot be any possible doubt about the identification. For the higher ones crystal splittings also have been used for identifying the levels. It is seen that in the crowded regions the mere position of a level is not enough for identification. Here the levels are very sensitive for the particular choice of the parameters, and the fact that the calculations are only approximate ones puts a limit to the accuracy one can expect.

The situation is similar for the other trivalent rare earths.[11-23] The references give in each case first the papers which give the most recent empirical data and then the ones containing the calculations. In all cases the first few multiplets have been identified beyond possibility of doubt. For the higher energies the situation is often so complicated that positive identifications cannot be made without a great deal of further study. Figure 8 gives a summary of the results obtained so far. Table I lists the parameters F_2 and ζ derived from these data.

Table I. Numerical Values of the Parameters F_2 and ζ

	Empirical			Theoretical[22]	
	F_2	ζ	ζ/F_2	F_2	ζ
Ce	—	640	—	453	830
Pr	305.4	729.5	2.39	477	980
	317.4	756.5	—	—	—
Nd	337	876	2.60	498	1130
Pm	346.0	1070	3.09	—	—
Sm	370	1200	3.2	532	1480
Eu	401	1320	—	—	—
Gd	405.4	1581.1	3.9	565	—
Tb	434	1705	—	—	—
Dy	420	1900	4.5	589	2310
Ho	450.1	2163	4.8	—	—
Er	429	2445	5.7	616	2830
Tm	451.1	2656	5.89	—	—
Yb	—	2882.9	—	642	3400

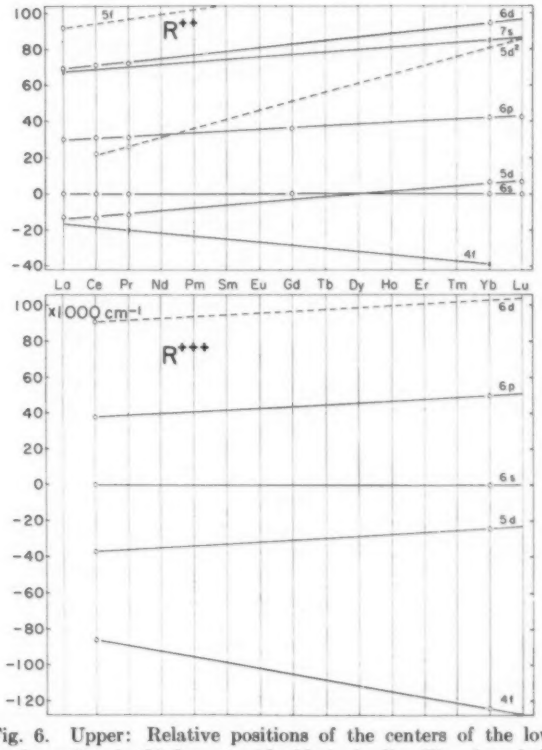

Fig. 6. Upper: Relative positions of the centers of the low configurations in third spectra (doubly ionized). The *nl* symbols refer to the optically active electron; e.g., 6*s* means $4f^{n-1}$ 6*s*. Lower: Same for fourth spectra (triply ionized).

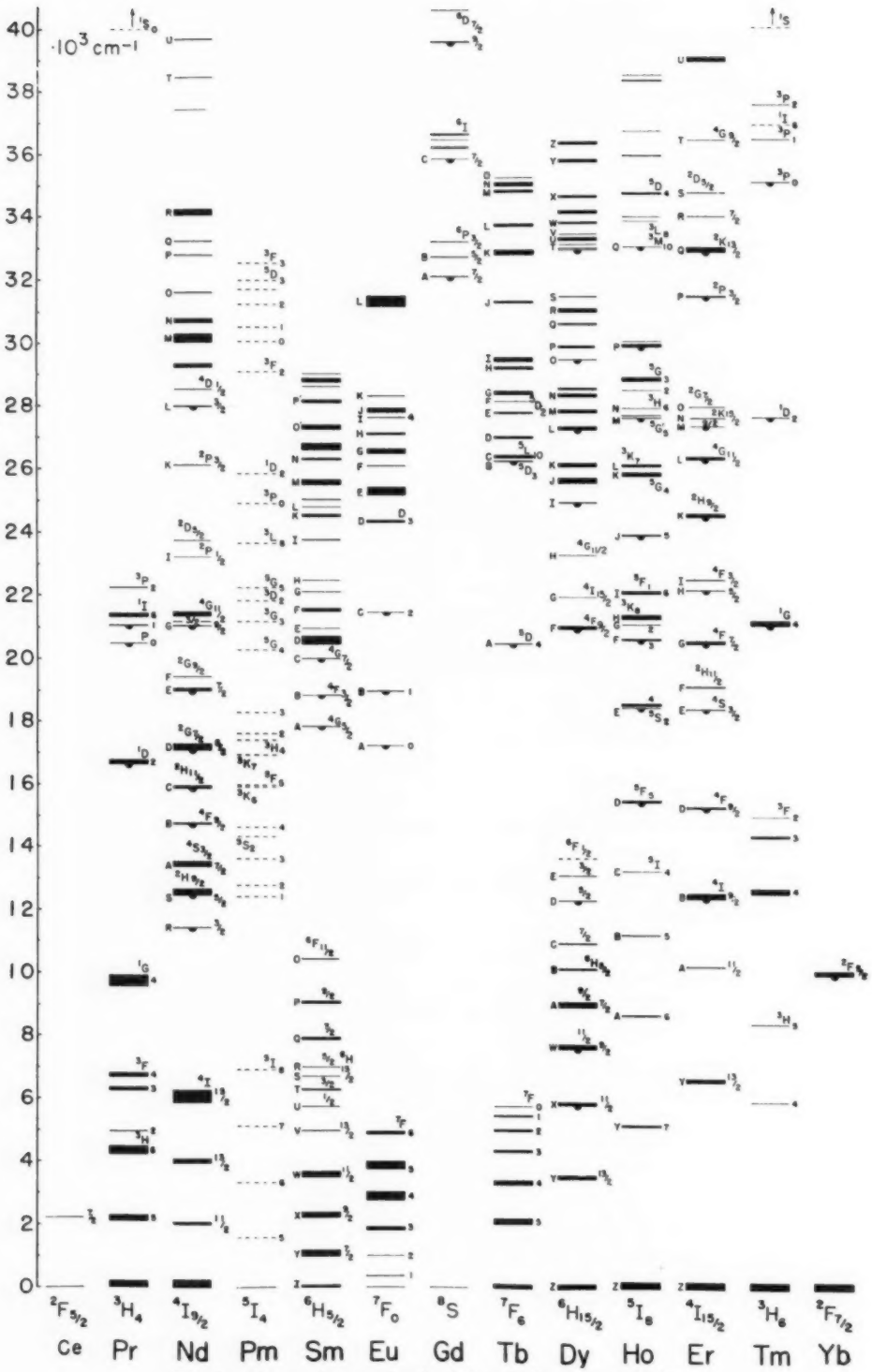

Fig. 8. Observed energy levels of the trivalent rare-earth ions.

The energy levels obtained in this way are, of course, those of the ion in a particular crystal lattice. Using the center of the Stark components eliminates the influence of the crystal field in first order. This, however, is not sufficient to obtain the free-ion levels with any high degree of accuracy. Comparison of the same levels in different lattices shows[6] that there may be shifts of several hundred cm^{-1} and we can trust the levels obtained from the crystal spectra to agree with the free-ion levels at most to this extent.

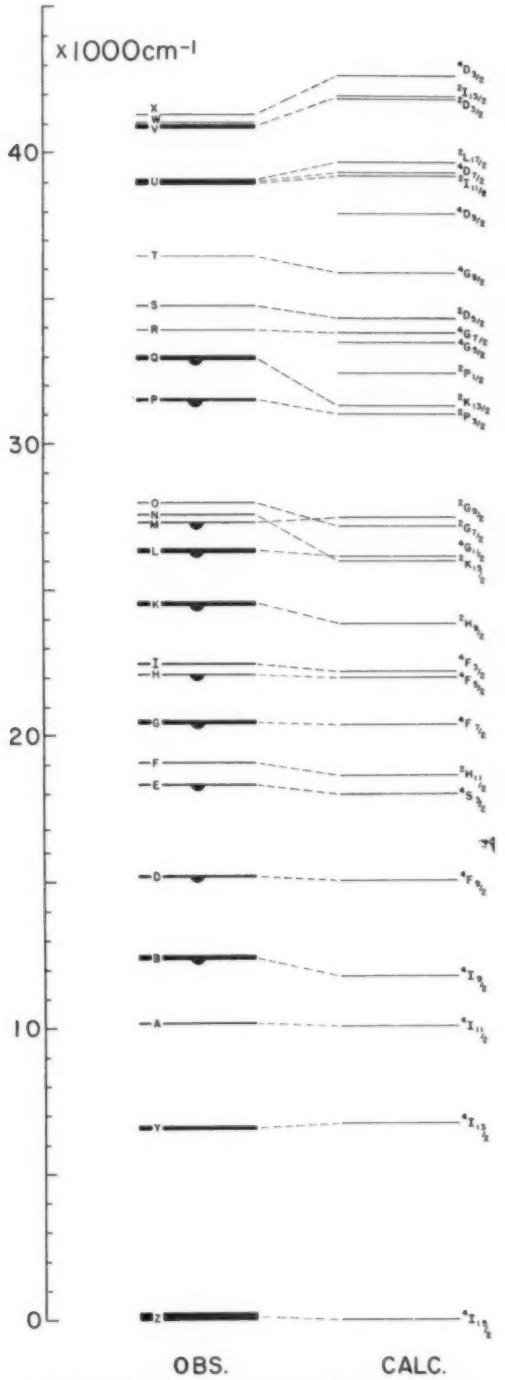

Fig. 7. Observed and calculated levels of Er^{3+}.

The configurations where not all outer electrons are in $4f$ orbits, such as $4f^{n-1}5d$ or $4f^{n-1}6p$, can be dealt with in similar fashion although the calculations are somewhat more involved as more parameters enter into the calculations. Figure 9 shows the situation for the $4f^{13}5d$ configuration of Yb^{2+}, and again it is seen that the comparison of the empirical levels with the calculated set gives a positive identification.[24]

Knowledge of the position and extent of the two lowest configurations $4f^n$ and $4f^{n-1}5d$ is particularly important as these two configurations may be expected to furnish the strongest lines.

Figures 10 and 11 give a survey of these configurations for the third and fourth spectra, respectively, obtained from preliminary empirical data and very approximate calculations. Because of the particular couplings involved we must in general expect the strongest lines to be transitions from the bottom of one configuration to the bottom of the other one, from the middle to the middle, etc. We see that for the fourth spectra all $5d \rightarrow 4f$ transitions must lie in the vacuum ultraviolet and shift from 2000 Å for Ce IV to 1000 Å for Yb IV. The $6p \rightarrow 5d$ transitions remain at about 1300 Å for all fourth spectra. The $6p \rightarrow 6s$ transitions, however, lie in the more easily accessible part of the ultraviolet and shift from 2500–2800 Å for Ce IV to 1700–2200 Å for Yb IV.

The situation for the third spectra is considerably different. For La III the $4f$ and $5d$ levels must practically coincide and the transitions between them lie

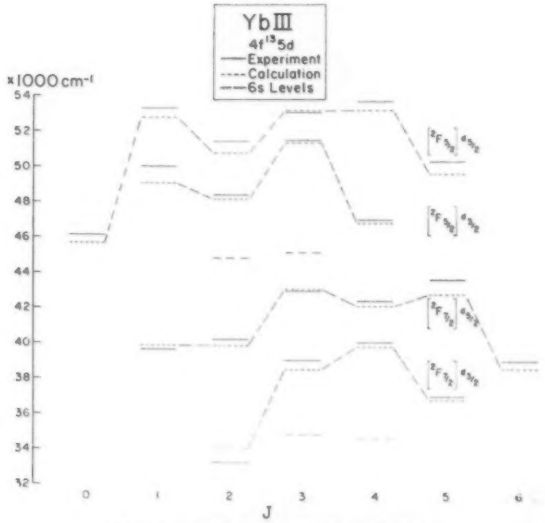

Fig. 9. $4f^{13}5d$ configuration of Yb^{2+}.

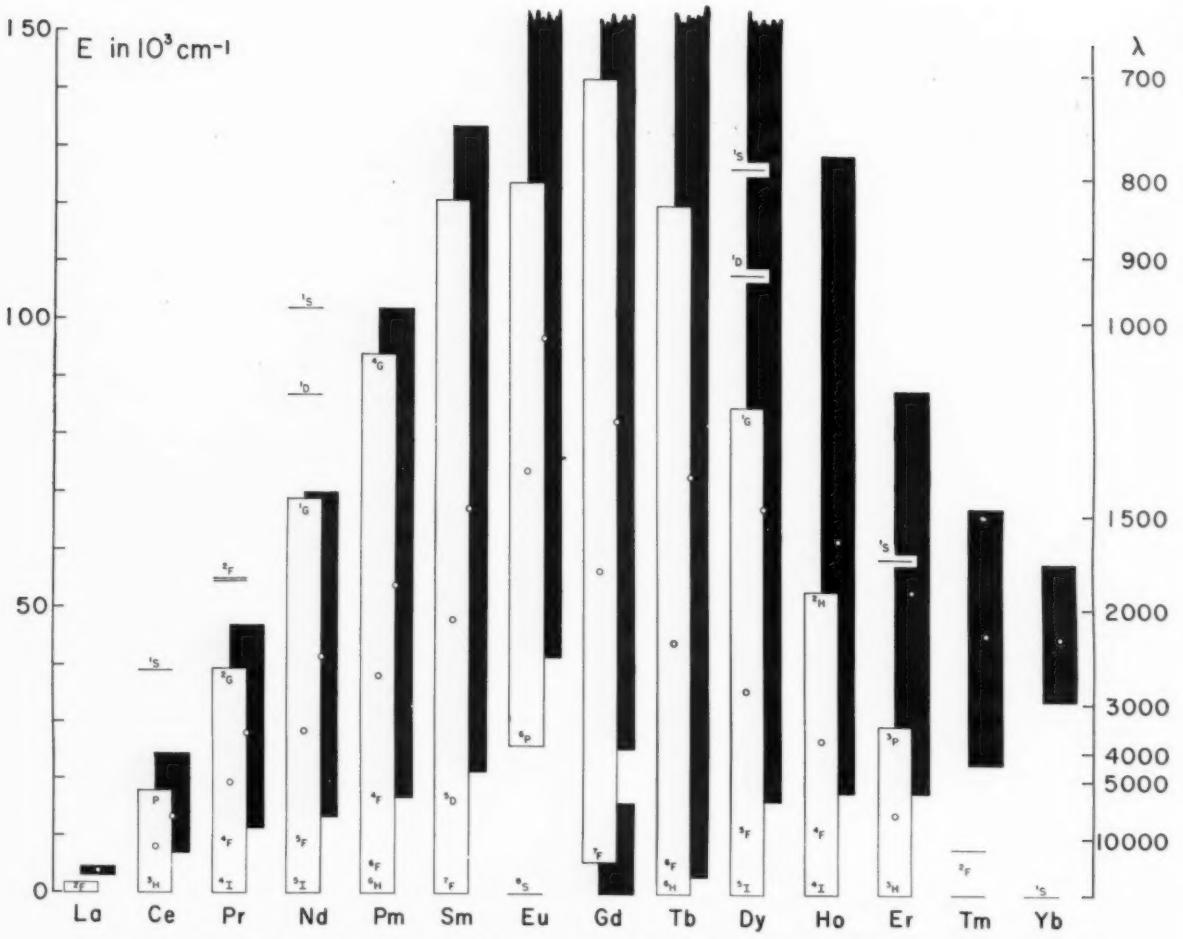

Fig. 10. Schematic diagram of the $4f^n$ (white) and $4f^{n-1}5d$ (black) configurations of the divalent rare-earth ions.

in the far infrared. For this reason they have not yet been found. They move apart with increasing Z, and the strong $5d \rightarrow 4f$ lines lie in the visible for Pr III and near 2000 Å for Yb III. Figure 10 shows that because of the varying width of the configurations the situation for the intermediate elements may be irregular. For Gd III for instance the strong lines must again be expected in the infrared, and a search for them (Callahan[25]) has revealed that they certainly cannot lie in the visible or ultraviolet. For the third spectra also the transitions between the other low configurations lie mostly in the visible or accessible ultraviolet where precise wavelength measurements can be made more easily.

We may now come back to the crystal spectra of the divalent ions. The sharp-lined crystal spectra in the visible and adjacent regions of the trivalent and divalent ions are due to normally forbidden transitions between levels of the $4f^n$ configuration. These are made possible, except for rare cases of magnetic dipole radiation, by the admixture through the crystal field of parts of opposite parity in the wave functions.[26] These transitions have f numbers of the order of 10^{-6} and would be completely blotted out if they occurred in the region of the allowed $5d \rightarrow 4f$ transitions. We have seen that for the trivalent ions the latter lie usually in the vacuum ultraviolet which leaves the visible and near ultraviolet free for the crystal spectra. Figure 10 shows that for the divalent ions the $5d \rightarrow 4f$ transitions usually reach into the visible which leaves much less room for the crystal spectra, and we must expect these chiefly in the infrared. Sm and Eu have long been known to form divalent ions. The fluorescence spectrum of Sm^{2+} is known in the extreme red and infrared[7] and resembles that of Eu^{3+} with all the energies roughly reduced by 20%. Something is also known of the spectrum of Eu^{2+}. Recently it has been found by Kiss[27] and others that in crystals that contain trivalent rare-earth ions these can be converted into divalent ions by irradiation with gamma rays. This makes it possible to obtain the

lowest levels of all the divalent rare-earth ions from crystal spectra data.

IV. The Interpretation of the Free-Ion Spectra

The energy levels derived from the crystal spectra are obtained without ambiguity and their interpretation is now possible without difficulties. The data so obtained are of necessity very limited, as they cover only the lower portion of the $4f^n$ configurations. While further studies in the ultraviolet may extend the known crystal lines somewhat, Fig. 11 shows that we cannot expect to go much further without coming in conflict with the strong continuous absorption to the $4f^{n-1}5d$ levels which may reach farther to the visible than the figure indicates because of the crystal field broadening of the $5d$ levels. Also other constituents of the crystal lattice may absorb in the far ultraviolet. In order to obtain a more complete picture of the energy levels, it is necessary to go to the free-ion emission spectra.

These as we have seen earlier are very complex

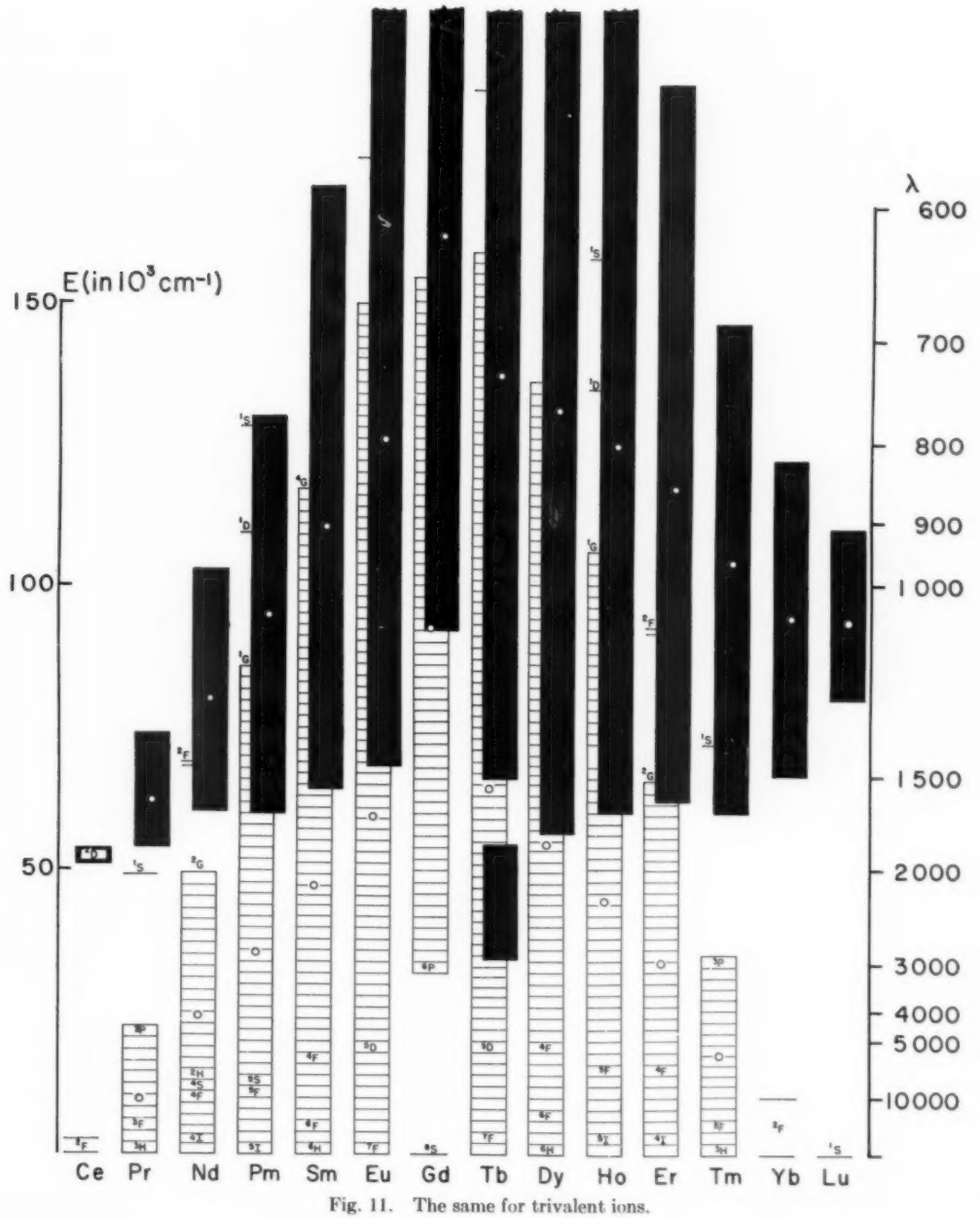

Fig. 11. The same for trivalent ions.

Table II. The Four Lowest Configurations of the Trivalent Rare-Earth Ions

R^{2+}	R^{3+}	n	Ground state	Number of levels $4f^n$	$4f^{n-1}5d$	$4f^{n-1}6s$	$4f^{n-1}6p$	Sum	Allowed transitions
—	La	0	$^1S_0$	1	—	—	—	1	—
La	Ce	1	$^2F_{5/2}$	2	2	1	2	7	8
Ce	Pr	2	$^3H_4$	13	20	4	12	49	324
Pr	Nd	3	$^4I_{9/2}$	41	107	24	69	241	5393
Nd	Pm	4	$^5I_4$	107	386	82	242	817	—
Pm	Sm	5	$^6H_{5/2}$	198	977	208	611	1994	306,604
Sm	Eu	6	$^7F_0$	295	1878	396	1168	3737	—
Eu	Gd	7	$^8S_{7/2}$	327	2725	576	1095	4723	—
Gd	Tb	8	$^7F_6$	295	3006	654	1928	5883	—
Tb	Dy	9	$^6H_{15/2}$	198	2725	576	1095	4594	—
Dy	Ho	10	$^4I_8$	107	1878	396	1168	3549	—
Ho	Er	11	$^4I_{15/2}$	41	977	208	611	1837	—
Er	Tm	12	$^3H_6$	13	386	82	242	723	—
Tm	Yb	13	$^2F_{7/2}$	2	107	24	69	202	3773
Yb	Lu	14	$^1S_0$	1	20	4	12	37	217

We have set ourselves the task of obtaining the four lowest configurations $4f^n$, $4f^{n-1}5d$, $4f^{n-1}6s$, and $4f^{n-1}6p$ of the third and fourth spectra as completely as possible. Experience with the spectra which have so far been analyzed[24,25,28] has shown that the electron in a $6s$ or $6p$ orbit (and even $5d$ for the heavier elements) is only loosely coupled to the core, which makes the so-called J_1j coupling scheme proposed by Racah[29] most appropriate. Strong transitions occur only when the core does not change and the orbital quantum number of the excited electron changes by ± 1. This has a marked influence on the appearance of the spectrum. As the Δl transitions are not much affected by the particular core value, there will be one such transition at approximately the same wavelength for each choice of core. For instance for the one-electron La III spectrum the $6p_{3/2} \rightarrow 6s$ and $6p_{1/2} \rightarrow 6s$ transitions occur at 3172 and 3517 Å, respectively.[30] In Ce III the corresponding $4f6p \rightarrow 4f6s$ transitions occur as groups centered near 3100 and 3400 Å; for Pr III at 3000 and 3350 Å. For Nd III we can, therefore, expect that the strong group of lines between 2900 and 3050 Å will belong to $4f^36p_{3/2} \rightarrow 4f^36s$ and those between 3200 and 3350 Å to $4f^36p_{1/2} \rightarrow 4f^36s$. In a similar way the strong group between 2050 and 2400 Å may be associated with $6p \rightarrow 5d$ transitions.

The number of levels in these configurations may be quite considerable, as Table II shows. The last column (for some elements) gives the number of lines that one would obtain if the parity and J-selection rules are obeyed, as well as $\Delta l = \pm 1$ rule for the electron that changes orbits. No other selection rules are used for this calculation, but many of the allowed lines may be so weak as to be unobservable. Nevertheless the table shows that the number of lines from these four configurations alone may be very large, and there are of course many other configurations that contribute to the spectrum. Under these circumstances one must proceed with the analysis with a careful plan in order not to be involved in a task that is too time-consuming for the results to be worth the effort.

In the first place it is essential to have as complete a wavelength table as possible with wavenumbers of the highest possible accuracy. The second step is to establish an empirical set of energy levels. Most of the labor of this step can be delegated to a computer. If nothing is known about the spectrum, the computer can be instructed to compute all wavenumber differences between the lines and list those that occur repeatedly within certain limits of accuracy. Many of these will be accidental coincidences, and in this step the accuracy of the wavenumbers is the decisive factor. If the tolerances are narrow, the chances for accidental coincidences become less. By examining all the significant differences, an empirical energy level diagram can be built up, the reliability and completeness of which depends on the extent and accuracy of the wavelength table.

As stated earlier, this process can be carried out in principle without any previous knowledge whatsoever

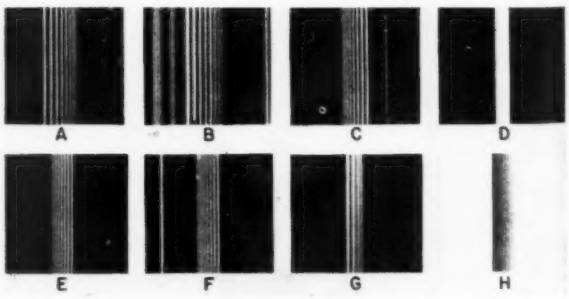

Fig. 12. Hyperfine structure of holmium lines. A–D, Ho II lines; E–G, Ho III lines; H, Ho IV line in crystal spectra.

of the structure of the spectrum. The procedure will, however, be greatly simplified if one knows what to expect. Since the energy differences between the lowest $4f^n$ levels of the fourth spectra and some of the third are known approximately from the crystal spectra, the computer needs to look in its first attempt only for differences within a few hundred cm^{-1} of these values. The $4f^{n-1}6s$ levels occur in pairs, the splitting of which can also be computed with considerable precision. The calculated energy levels will then limit further the range of differences that have to be examined with a great saving in effort and computer time. This search is further aided if one can limit it to a restricted wavelength region as discussed above. Careful studies of excitation variation such as shown in Fig. 1 are also helpful in reducing the number of lines to be handled. Not only is it possible to specify the ionization stage, but also the approximate excitation level for a given ion. This allows the upper electron configuration from which the particular transition occurs to be identified. If enough care is taken, information may be obtained even about the position of the level within the configuration. If necessary, electronic time-decay techniques may be used.[31] After successive efforts of this kind a fairly extensive set of empirical levels can be constructed.

The next step is the interpretation of the levels, which means assigning quantum numbers to them and correlating them with the levels to be expected theoretically. The most important of the quantum numbers is the angular momentum J. This often can be established from the selection rule $\Delta J = 0, \pm 1$ which must be satisfied by all lines of the free-ion spectrum. Under favorable circumstances this establishes relative J values of all the levels, which can be turned into absolute values if the J for one level is known. This is always the case for at least the lowest level which is known by Hund's rule. (Highest L of highest multiplicity, lowest J of this multiplet before Gd IV, highest J after Gd IV.)

For the crystal spectra, the Zeeman effect is useful in providing additional important information, but with these higher ionization stages of the free ion the situation is not so favorable. The spectra are very crowded and the lines somewhat broadened by the violent discharge conditions needed to produce them. Furthermore, the strong J_1j coupling makes all $6p \rightarrow 6s$ transitions for instance look very similar. Obtaining reliable Zeeman effects under such conditions would add greatly to the burden of wavelength measurements and analysis. We have found that the other methods for the analysis described here give such definite and positive results at least for the low configurations that there has been no need for Zeeman effect data.

Another important aid for the analysis is the presence of hyperfine structure. This is simplest when there is only a single odd mass number isotope, as is the case for Pr, Tb, Ho, and Tm, particularly with Pr and Ho because of the large value of the nuclear magnetic moment. The magnitude of the hyperfine structure indicates whether or not an s-electron is present and can give other information about the nature of the configuration. Figure 12 shows a few examples of resolved hyperfine structure in the spectrum of holmium. The number of the components gives the value of J if it is below the nuclear spin. The intensities and relative spacing of the components indicate the J values in general, and other important information on the nature of the levels can be obtained from the hyperfine structure.

Obtaining similar information for other elements would require separated isotopes. For these, isotope shifts also could be used for the identification of configurations. So far it has not been necessary to use separated isotopes, but later they may be needed to give enough information to decide doubtful cases.

The most valuable and important aid for the analysis of these complicated spectra has, however, been the comparison of the empirical levels with the calculated ones and this, in general, leads to a positive and unambiguous identification of the levels. While matrix elements for the f^n configurations are now available, in general the $f^{n-1}l$ ones are not. The computation of these is a straightforward, but very tedious process. Here again, we may make use of high-speed computers, and these matrices are being compiled as needed.

V. Results So Far Obtained

While the initial incentive for the investigation was the desire to know the $4f^n$ configurations of the free-ion levels of the trivalent rare earths in order to have a basis from which to evaluate the influence of the crystal field, most results have been obtained so far with the spectra of the divalent ions.

The trivalent $4f^n$ levels can only be obtained through the allowed $5d \rightarrow 4f$ transitions which lie in the vacuum ultraviolet, and so do the $6p \rightarrow 5d$ transitions which can be used to confirm the $5d$ configuration. At the present time a new large vacuum spectrograph for our laboratory is under construction which is to be ready for use during the summer of 1963. In view of this it is undesirable to use the much less accurate vacuum ultraviolet wavelengths now available to us. For this reason so far only parts of the Pr IV and Yb IV spectra have been analyzed.

The situation is much more favorable for the third spectra, as the most important lines lie in the more easily accessible region of the spectrum. Moreover, the

crystal spectra of the divalent ions also have become of increasing interest recently.

At the present time the goal of obtaining the four lowest configurations has been substantially reached by Sugar[28] for Pr III and by Bryant[24] for Yb III. Less complete results have been obtained so far for Gd III by Callahan.[25] For this ion the configurations are particularly unwieldy, and it cannot be expected that the four ground configurations which contain together nearly 6000 levels can be obtained with anything even remotely approaching completeness. While the parts of the $4f^7 5d$, $4f^7 6s$, and $4f^7 6p$ configurations based on the ground term ^8S of $4f^7$ are known, nothing is known yet about the $4f^8$ configuration. As Fig. 10 indicates for Gd III, the $4f^8$ and $4f^7 5d$ configurations must be expected very close together, so that the principal lines connecting them must be expected in the infrared. This is apparently true, for none of these lines has been found in the visible or the easily accessible parts of the infrared.

Work on the third spectra of the following elements is in various stages of progress in our laboratory. Nd III (K. V. Narasimham), Sm III (F. L. Varsanyi), Ho III (J. H. McElaney), where the large hyperfine structure is very valuable, Er III (J. Becher), and Tm III (G. Gompertz). Work on the remaining elements will be taken up as soon as an opportunity arises. Because of the very large number of lines involved progress is necessarily slow even when all modern aids are available.

It should be emphasized that the preceding article is not a general account of the spectra of the doubly and triply ionized rare earths which would have been impossible in the allotted space, but essentially an outline of the work being carried out in this field at Johns Hopkins University.

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Recent Work on the Second Spectra of Some Iron Group Elements

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Recent results from the analyses of the spectra V II, Mn II, and Ni II carried out at the Institute of Optics, Madrid, are briefly described. The agreement between these experimental results and the theoretical calculations of energy levels is pointed out. Some new work on Mo III and Rh III is also mentioned.

Introduction

During the past ten years one of the most active fields of research in our laboratory has been the excitation, description, and analysis of the second and third spectra of several elements of the so-called "iron group". Papers on the second and third spectra of vanadium, manganese, and nickel[1-8] have already been published but many unpublished results are still available.

The increasing facilities of electronic computers during the past decade have allowed for great improvement in the calculation of energy levels of complex atoms and ions. The group at the Hebrew University, under G. Racah's direction, has been especially active in this field. Many theoretical results about the fundamental configurations $3d^m$, $3d^{m-1}4s$, $3d^{m-2}4s^2$, and $3d^{m-1}4p$ of the second spectra of the iron group elements have been published.[9,10]

Some of these theoretical results have confirmed our previous experimental analyses, and some have been very valuable in correcting past errors in the interpretation of spectral regularities. Finally, some results have become very important in predicting the energies of unknown levels, and thus a great help in finding them empirically.

A general account of the experimental results recently obtained for the spectra V II, Mn II, and Ni II will be presented in this paper with special reference to the levels for which theoretical calculations have been made. A more detailed description of the particular analysis of each of the spectra treated here will be presented in future publications.

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Experimental Details

The spectra discussed here were observed under different types of excitation and in different laboratories. Hollow cathode spectra of vanadium, manganese, and nickel were observed several years ago by using the facilities at the Institute of Physics, Lund (Sweden). Arc and spark spectra of manganese were obtained at Palmer Physical Laboratory, Princeton (U.S.A.), and arc and spark spectra of vanadium and nickel were also excited at our laboratory at the Institute of Optics (Madrid). The spectra were produced by means of concave gratings in different mountings but in all cases giving reciprocal dispersions of the order of 5 Å/mm or better, allowing wavelength determinations with probable errors of only a few thousandths of an angstrom in most cases.

Results

The spark excitation proved very useful for observing the most important part of each spectrum, namely, the lines due to transitions between the fundamental terms of the configurations already mentioned. Hollow cathode spectra were especially valuable for the excitation of series,[5] and the arc spectra were very useful for studying transitions among high levels of the fundamental even and odd configurations. This sort of excitation proved the most fruitful, especially in the case of Mn II, where many levels of the fundamental configurations still needed experimental evidence.

Since most of the lines observed in the spectra of stars correspond to transitions between levels of the fundamental configurations, the new Mn II lines observed in the arc spectrum of manganese have a straightforward application for the interpretation of

Table I. New Mn II lines of Astrophysical Interest (Iglesias)

λ (Air)	Int.	λ (Air)	Int.	λ (Air)	Int.
6682.42	10	4503.20	10	4180.033	20
6677.71	1	4500.55	10	4177.618	1
6609.26	5	4497.95	2	4177.470	20
6571.74	1	4478.644	100	4174.31	100
6565.71	2	4441.991	30	4172.278	5
6497.02	10	4434.063	60	4172.125	5
6475.38	12*h*	4403.505	60	4171.509	50
6457.26	15*h*	4393.385	60	4171.042	40
6452.89	1	4391.955	5	4140.44	20
6267.14	10	4386.567	5	4136.95	60
6240.94	5	4385.733	10	4136.24	2
6190.97	2	4379.63	80	4110.62	30
6101.36	1*h*	4377.74	50	4109.20	1
6045.36	1	4371.893	1	4104.995	50
6040.36	2	4365.22	100	4100.003	10
5978.58	10	4363.259	50	4094.41	5
5963.27	3	4356.63	80	4087.90	5
5943.91	5	4348.39	200	4085.39	5
5901.72	10	4346.39	50	4083.66	200
5826.29	10	4345.580	50	4081.455	20
5752.23	10	4343.982	500	4000.035	20*h*
5578.15	30	4342.579	30	3995.31	15*hd*?
5570.51	30	4338.350	60	3994.120	10
5561.38	1	4336.966	30	3986.59	5
5559.05	50	4331.685	20	3975.740	20
5511.48	3	4326.633	500	3970.240	20
5509.97	3	4325.030	100	3967.989	20
5501.12	3	4318.52	60	3953.59	5
5446.48	5	4317.717	30	3952.42	20
5421.92	10	4316.77	5	3943.858	30
5307.35	10*h*	4316.19	10	3943.603	20
5251.82	10*h*	4314.366	20	3941.216	40
5177.648	10	4308.16	100	3930.974	20
5123.32	10	4302.96	40	3926.12	5
5107.090	3	4300.24	( )	3917.324	30
5102.52	8	4291.46	15	3905.465	30
4921.26	20	4289.60	30	3902.378	10
4920.48	5	4288.07	30	3898.069	100
4851.46	8	4282.477	60	3897.616	100
4847.60	50	4282.265	20	3889.132	20
4842.36	10	4281.94	50	3879.004	60
4839.775	5	4275.87	15	3863.402	40
4830.08	10	4267.85	10	3859.207	10
4811.62	10	4260.46	40	3857.91	3
4806.86	100	4253.12	10	3848.57	10*hd*
4791.81	20	4251.735	150	3844.167	200
4764.73	100	4247.952	80	3843.33	( )
4755.733	200	4245.94	5	3839.052	20
4749.15	10	4244.256	150	3831.45	( )
4742.95	10	4242.923	30	3825.04	30
4738.30	100	4242.336	100	3817.258	80
4737.96	1	4240.39	20	3812.519	10
4730.38	40	4239.189	60	3812.21	10
4727.86	20	4238.78	80	3801.142	10
4717.29	10	4237.870	20	3800.240	2
4702.72	5	4232.84	3*h*	3796.440	50
4689.56	10	4223.61	1	3789.52	5
4610.59	1	4215.54	1*h*	3786.38	1
4525.39	20	4207.229	30	3783.910	20
4525.32	20	4207.10	1	3778.320	200
4519.24	20	4205.396	100	3775.05	5
4518.964	200	4200.289	60	3773.56	8
4509.21	2	4184.467	50	3769.06	8
3767.94	10	3662.13	8	3444.33	5
3767.509	30	3656.492	100	3443.058	5
3764.853	30	3655.55	5	3442.53	20
3763.74	( )	3655.27	40*d*?	3441.347	10
3755.203	60	3654.560	5	3438.038	10
3754.77	1	3654.43	1	3436.27	5
3752.425	20	3653.444	20	3431.13	10*h*
3752.001	5	3650.39	1	3429.04	20
3751.737	20	3649.84	20	3428.150	80*d*
3750.477	200	3644.95	1	3427.65	20
3749.84	1	3643.42	5	3424.911	2
3748.780	50	3636.04	1*h*	3421.572	10
3744.71	5	3635.70	2*h*	3421.461	20
3743.386	100	3632.456	10	3419.58	10
3740.298	20	3631.419	100*d*?	3413.276	1
3735.133	15	3628.647	10	3407.68	1
3731.14	1	3627.478	200	3407.11	2
3730.068	30	3627.18	1	3395.000	8
3729.488	40	3626.83	5	3394.841	80
3728.716	( )	3622.65	10	3394.386	60
3727.245	20	3622.003	10	3392.46	8
3725.280	40	3614.49	30	3391.87	10
3724.806	60	3600.35	1	3391.26	1
3723.31	40	3591.38	5	3390.074	15
3719.48	1	3583.042	10	3387.816	20
3717.515	40	3576.422	5	3387.749	80
3717.097	40	3563.115	50	3386.15	5
3715.267	100	3560.18	2	3384.81	80
3714.775	30	3519.66	2	3383.582	( )
3713.630	30	3513.08	10	3382.09	2
3710.970	80	3511.383	20	3381.675	80
3709.855	20	3510.986	40*d*?	3378.72	20
3708.058	20	3510.704	3	3377.981	15
3706.886	50*d*?	3509.935	100	3376.412	20
3705.277	2	3508.315	30	3376.28	50
3703.960	30	3508.204	8	3374.919	30
3703.288	15	3501.44	20*h*	3367.72	10
3702.790	40	3499.501	20	3366.108	80
3702.170	40	3495.024	2	3366.03	30
3701.389	80	3494.377	20	3363.019	300
3700.518	30	3494.157	20	3362.412	40
3695.920	100	3492.276	80	3359.614	10
3691.848	60	3489.296	10	3358.411	100
3691.68	1	3486.992	5	3349.50	100
3690.65	2	3485.395	15	3348.24	40
3690.320	100	3484.661	2	3343.01	25
3689.948	10	3483.819	20	3342.330	30
3688.659	8	3472.214	30	3341.82	80
3686.79	15*d*	3469.20	30	3340.40	10
3686.216	40	3468.527	8	3339.59	10
3686.136	30	3468.380	15	3333.115	40
3685.90	1	3467.781	5	3332.366	40
3683.618	100	3466.976	10	3332.274	30
3682.56	15	3466.594	15	3331.532	200
3682.07	( )	3465.519	3	3328.415	100
3678.56	5	3464.928	10*h*	3328.003	200
3678.318	20	3462.342	20	3327.27	20
3674.312	40	3461.462	20	3326.42	30
3673.88	5	3455.510	20	3326.17	10
3670.90	1	3454.500	10	3326.069	30
3668.008	30	3451.549	10	3325.83	10
3667.33	10	3446.26	1	3324.118	100*d*
3665.81	1	3444.521	5	3322.92	30*d*

continued

Table I—continued

λ (Air)	Int.	λ (Air)	Int.	λ (Air)	Int.
3321.999	40	3205.259	30	3079.38	20
3320.57	60	3204.749	15	3076.833	10
3313.916	20	3204.12	10*h*	3076.330	30
3312.783	20	3202.617	30	3075.106	20
3308.461	40	3199.522	20	3074.04	10
3307.810	100	3198.261	2	3072.875	2
3306.464	20	3198.145	20	3072.50	1
3303.427	10	3196.244	40	3070.821	80
3301.50	2	3194.339	20	3069.73	2
3301.25	5	3193.578	10	3065.709	10
3299.11	10	3192.64	5	3063.31	3
3298.029	80*d*	3190.53	5	3062.511	40
3295.533	20	3189.233	40	3059.772	20
3295.36	5	3186.724	15	3057.64	10
3291.723	10	3184.818	40	3056.709	30
3291.420	10	3184.035	20	3055.885	5*h*
3290.070	10	3183.09	2	3054.68	5
3289.002	40	3173.463	40	3052.18	2
3288.288	20	3172.680	10	3048.39	3
3287.222	80	3170.800	50*d*?	3046.86	5
3287.13	20	3169.914	50	3044.06	20
3286.613	20	3168.216	30	3033.574	100*d*
3286.040	10	3159.30	30*d*	3033.24	2
3285.18	2	3156.43	25	3032.00	10
3284.945	40	3155.44	10	3026.86	10
3284.12	2	3150.426	30	3025.198	40
3283.456	20	3149.931	30	3024.49	15
3283.32	2	3146.116	30	3023.28	2
3280.078	80	3142.29	50	3021.27	5
3276.753	200	3139.844	40	3021.10	1
3275.009	10	3134.666	40	3020.610	15
3274.043	30	3131.020	20	3020.485	30
3273.791	15	3128.631	30	3019.72	40
3273.624	10	3127.946	20	3018.552	2
3272.72	20	3126.734	30	3015.854	15
3272.138	20	3125.228	80	3014.849	20
3271.347	20	3123.688	40	3013.662	20
3271.174	40	3120.564	30	3011.97	10
3271.010	10	3113.23	10	3005.142	10
3270.658	100	3111.08	10	3003.22	5
3264.171	150	3109.816	10	3002.87	20
3261.869	20	3103.958	1		
3261.75	1	3102.99	1		
3257.53	20	3102.564	15		
3256.62	20	3099.302	20		
3255.22	2	3095.992	20		
3252.720	30	3094.82	1		
3252.380	10	3093.142	5		
3251.319	30	3092.94	1		
3246.37	8	3089.40	1		
3235.669	5	3088.53	5		
3225.628	30	3086.972	40		
3208.842	10	3085.737	20		
3268.42	2	3084.712	30		

stellar spectra. This has already been done successfully at the Lick (U.S.A.) and La Plata (Argentina) Observatories by using part of our list of new wavelengths. Therefore, we think it of special interest to publish a table of all the new Mn II lines that have been observed in the region most important to the astrophysicist. Table I is such a simplified list, from 3000–6000 Å, including all the observed lines with their estimated intensities but without any indication of their classification. In fact about 90% of the lines in the table have been classified as transitions between levels discovered in the course of this work.

The arc spectra of vanadium and nickel did not produce such an extensive list of new lines, mainly because the fundamental configurations of these ions have relatively few energy levels, most of which (and therefore the transitions among them) were already known. The list of lines belonging to V II and Ni II have been considerably extended at wavelengths greater than 5000 Å by means of the hollow cathode observations, but those lines are of less general interest. Most of them arise from transitions between series levels, and in the case of V II, have led to the first experimental determination of the ionization potential. The value obtained from the study of the fundamental levels of three members of the *nf* series is 118,400 ± 100 cm^{-1} (14.7 eV), which agrees well with the value predicted by Russell[11] from a general study of the second spectra of this group.

From these collections of new experimental data it has been possible to extend considerably the number of empirically determined energy levels of Mn II, V II, and Ni II. The main results of the work can be summarized as follows. Our knowledge of the structure of these ions has been greatly improved with the determination of energy levels belonging to the fundamental configurations in good agreement with the theoretical calculations of Racah, Shadmi and Spector. Previous experimental Mn II energy levels that did not agree with the theoretical calculations have been found spurious. New energy levels, in agreement with the theory have been determined to replace them. The Zeeman-effect interpretation of the spectrum Mn II has also confirmed the theoretical *g* values calculated by Racah and Shadmi. Series have been found or extended, thus giving new calculations or recalculations of the ionization potentials of Mn II and V II. The analysis of Ni II is still in progress. Table II shows a summary of our contribution to the analysis of the fundamental configurations of the three spectra described in this paper.

Apart from the results in Table II the spectra Mn II and V II have also produced many new series levels, and we hope that the analysis of Ni II, still in progress, will also prove fruitful in this respect. Detailed descriptions of the analyses with lists of all classified lines and new energy levels will be published in *Anales di Fisica y Química.*

In view of the success of the work just described, and of the confidence that one can have in the theoretical calculations mentioned, a revision of the analyses of the

Table II. Numbers of Energy Levels of the Fundamental Configuration of V II, Mn II and Ni II

Configuration		V II	Mn II	Ni II
$3d^m$	Theory	34	34	2
	Exp. before	32	19	2
	Exp. now	33	31	2
$3d^{m-1}4s$	Theory	38	74	16
	Exp. before	37	29	15
	Exp. now	38	62	15
$3d^{m-2}4s^2$	Theory	9	34	19
	Exp. before	1	5	—
	Exp. now	8	5	5
$3d^{m-1}4p$	Theory	118	213	45
	Exp. before	109	66	43
	Exp. now	109	177	43

spectra Mo III and Rh III has been already started at our laboratory. There is an urgent need for both, since Mo III is a rather poorly known spectrum. F. R. Rico, from our group, was recently able to observe this spectrum under very favorable conditions. Rh III, observed by Shenstone several years ago, was later misinterpreted. Most of the resulting energy levels listed in the "Atomic Energy Levels" tables are unreal. This was already pointed out by Racah, and now the analysis just begun confirms this point of view, since many new levels can be found to replace the unreal ones. The new levels are both in very good agreement with the theoretical calculations[12] and with the good experimental observations of Shenstone.

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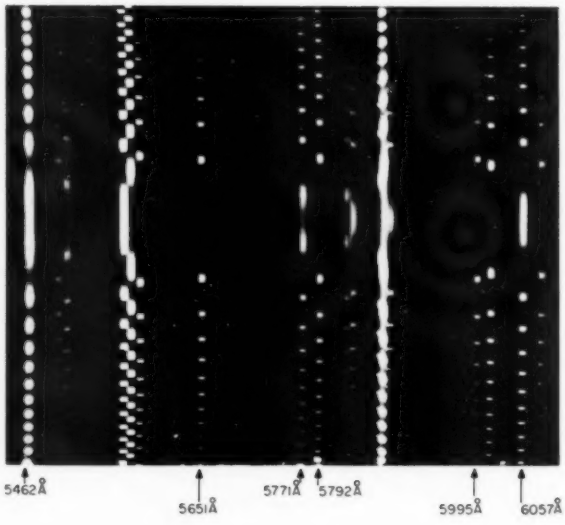
Cover Photo

Appearing on this month's cover is an interferogram of the spectra of Kr^{86} and Hg^{198} in the region from about 5450–6100 Å. This was obtained by Victor Kaufman of the Spectroscopy Section of the National Bureau of Standards during the course of the study which was published as "Wavelengths, Energy Levels, and Pressure Shifts in Mercury 198" in the August 1962 issue of the *Journal of the Optical Society of America*. The Kr^{86} lines were emitted from the capillary of a hot-cathode discharge lamp which was operated within the conditions recommended by the International Committee on Weights and Measures. The source was a Meggers Hg^{198} water-cooled electrodeless discharge lamp containing argon at a pressure of 3 mm Hg and was excited with a 2450 Mc/sec microwave unit. The plate was obtained by crossing a large Gaertner quartz prism spectrograph with a 100-mm Fabry-Perot interferometer. A partially reflecting mirror was used to pass simultaneously the radiation from both sources through the interferometer and spectrograph.

The sharpest spectral lines produced by conventional (i.e., excluding atomic beam and laser) sources are emitted by these two discharge lamps. The Kr^{86} line at 6057 Å is the international standard of length, the meter being defined as 1,650,763.73 vacuum wavelengths of this radiation. The wavelengths of the other two Kr^{86} lines noted have been most often compared with that of the standard and are probably the most accurately measured of all spectral lines. The green and yellow lines of Hg^{198} at 5462, 5771, and 5792 Å, however, are probably the most frequently used interferometric standards. Thus, this month's cover plate shows some of the presently most useful spectral lines, especially in metrology.



The Observation of Extraphotographic Infrared Atomic Emission Spectra

Curtis J. Humphreys and Edward Paul, Jr.

The extension of observation of atomic line emission spectra into the extraphotographic infrared region by high-resolution methods has been accomplished by procedures now well established but which have not found widespread application. Owing to the nonintegrating character of radiometric detecting devices, the observations are always energy-limited. This handicap may be overcome by a threefold approach: utilization of a fast optical system; optimizing the detecting and amplifying system; and developing sources of maximum energy output consistent with the character of the spectrum to be studied. Successful systems for use with a high-resolution grating spectrometer are described. Examples are given of the extension of the observation of several spectra to a fairly easily attainable limit of 4 μ by use of lead sulfide detectors designed for liquid nitrogen cooling.

I. Introduction

The remarkable success that was achieved in the observation and interpretation of atomic emission spectra, during the period of intense activity in that area of research, is accounted for, in no small part, by the fact that the preponderant radiant energy associated with such spectra is bracketed within the spectral range accessible to the relatively easy techniques of photographic recording. Included in this range is the vacuum ultraviolet, the ordinary ultraviolet, the visible, and the near-infrared accessible to dyed emulsions, the latter terminating under optimum conditions near 13,000 Å. It must be pointed out, however, that the extraphotographic region does include a significant part of the energy of atomic emission spectra, in spite of generally small transition probabilities and the classical laws of radiation formulating the dependency of intensity upon wavelength. Also, the frequency span of significant infrared energy is long even if one includes only the relatively small part of it that has been explored by use of the most sensitive detectors. To illustrate the latter point, suppose we consider the visible region between 4000 and 8000 Å as one octave. Using this measure, it turns out that there are three and one-half octaves between an arbitrary point of 1000 Å in the vacuum ultraviolet region and 12,000 Å in the infrared near the limit of photographic response. The same octave interval for the extraphotographic infrared region extends from 12,000 to 128,000 Å reaching slightly beyond the wavelength of the first line of the sixth series of hydrogen, 123,684 Å, first observed by one of the authors.[1]

The occurrence of transitions of extremely high intensity beyond the photographic limit is somewhat unusual, owing to the fact that relatively low combining levels generally show a greater separation than higher ones. This situation of course aggravates the difficulties of observing in that region, which are mainly related to availability of radiant energy in relation to responsivity of detecting systems. Certain classes of transitions occurring beyond 1 μ are of exceptional intensity. The best examples are the diffuse doublets and triplets —the transitions between terms arising from configurations involving p and d valence electrons of lowest total quantum number in the heavier alkalies, rubidium and cesium, and all of the alkaline earths. Observation of these lines by Paschen and Götze[2] is part of the early history of the subject.

Other noteworthy classes of intense lines are those of the noble gases that represent transitions between levels originating in the configurations p^5p and p^5d. These are fairly large groups, the strongest line from each group being

argon	13,718 Å,
krypton	18,167 Å,
xenon	55,738 Å.

These lines are of considerable importance as standard wavelengths and in metrological applications, particularly since isotopes of single mass number, Kr^{86} and

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Xe^{136}, are available which yield lines without isotopic or hyperfine structure.

The history of the investigation of atomic emission spectra by radiometric methods and a compilation of references on the results of such observation have been reported by one or both of the authors in a series of publications[3–6] beginning with the presentation at the Rydberg Centennial Conference in 1954. In each instance it was noted that activity in this specialty is divided into two distinct periods separated by more than thirty years. The first period, ended about 1914, is represented almost entirely by the work of Paschen and his pupils using thermal detectors, and is reported in the monograph by Paschen and Götze.[2] The story of the early period is also told in most interesting fashion by Randall in his Ives Medal Address.[7] The second period is associated with the development of an essentially new art of observation, made possible by the utilization of photoconductive detectors which became available shortly after the end of World War II.

The essential purpose of this paper is to describe the experimental devices and methods that this category of radiation-sensing elements has brought into being, with particular reference to the observation of atomic emission spectra. It is well known, of course, that photoconductive detectors and similar solid-state quantum devices have found extensive application in the study of overtone and combination bands under high resolution. This paper is concerned almost entirely with work of the authors, which is the only currently active program of investigation of extra-photographic infrared atomic spectra in the U.S.A. Other such efforts, both in this country and in Europe, particularly by I. Johansson at the University of Lund, Sweden, by L. F. H. Bovey at the Atomic Energy Research Establishment, Harwell, U.K., and by G. Hepner at the Sorbonne, Paris, are mentioned in the referenced review articles. Attention is directed to only one such example in the U.S.A., namely, the program at Northwestern University associated with the names of Russell A. Fisher and Edson R. Peck. That program coincided with the early period of the senior author's incursion into this field at the National Bureau of Standards, but the two programs were completely independent.

II. Direct Observation of Spectra by High-Resolution Scanning Methods

The essential point of difference between radiometric and photographic registration of an energy signal lies in the integrating feature of the latter. Since radiometric recording must depend on the strength of signal alone without integration, the problem must be approached from the point of view of three possibilities of optimizing the available signal. In the order in which they are discussed here these possibilities are: (1) utilization of fast optical systems in the spectrometer and matching accessories for handling the energy at entrance and exit; (2) improvement of detecting and amplifying systems; and (3) building up the radiant energy output of sources to the greatest extent possible consistent with maintenance of spectral characteristics.

The opportunity to extend the observations of atomic emission spectra beyond the long-wave limit of photographic response provided one of the principal incentives to the senior author to resume radiometric work in 1943. The acquisition of a program of evaluation of infrared-sensitive detectors at the National Bureau of Standards a few years later made detectors available so that the spectroscopic program could be started.

Optical Equipment for Observation of Infrared Atomic Emission Spectra

In keeping with the objective of extending the observations of atomic spectra into the extraphotographic infrared region, while at the same time maintaining resolution comparable to that realized in photographic recording, it was obvious that a high quality grating must be featured in the instrument design.

The spectrometer used in essentially all of the investigations reported by the authors was designed and built at the National Bureau of Standards during the period of association of the senior author with E. K. Plyler. It has been illustrated and described briefly in two publications.[8,9] Actually, in designing an instrument for use with lead sulfide detectors, adaptation for observation of either line emission or molecular absorption spectra was kept in mind. The layout of the instrument resembles the Perkin-Elmer Model 12, except that all dimensions are much larger and a grating is used as the dispersing element. The original grating was a Johns Hopkins ruling on an aluminized blank, 23 cm in diameter, ruled 600 lines/mm. the lines about 13 cm long extending over 19 cm. The grating was blazed for the region near 1.5 μ. This grating has since been duplicated and we have also obtained one of the same dimensions, ruled with 300 lines/mm. Having in mind the equation for the Littrow mounting for the ideal condition of superposed entrance and exit slits, $\lambda = 2d \sin\theta$, the limiting first-order wavelength observable with a 600 lines/mm grating at grazing incidence is 3.33 μ. With the duplicate of the first grating it has been possible to observe an argon line at 33,284 Å. Obviously the upper limit for a 300 lines/mm grating is 6.66 μ. The Littrow mirror is a paraboloidal surface 18 cm in diameter and 102 cm in focal length, 10° off-axis. The single-mirror off-axis Littrow system has the advantages of extreme simplicity and relative freedom from optical aberration if the portion of the slit from which the mirror is illuminated is shortened to approximate a point. This condition may be satisfied compatibly with efficient illumination by using small-bore

tubular sources in end-on presentation Since sources of tubular design are generally used for atomic emission work, the off-axis mounting lends itself admirably to the same utilization. The detector is placed with respect to the exit slit at the conjugate focus of an ellipsoidal mirror 18 cm in diameter having a 7 to 1 focal ratio and used in the on-axis arrangement. The large aperture minimizes the effect of shadowing by the detector mounting and the reduced image size is desirable for optimum detector performance. An important feature of this instrument is the relatively small aperture ratio, about $f/6$. This feature has made possible the discovery of many faint lines, and, more than anything else, has been responsible for the success of the program on interferometric determination of wavelengths in the infrared.

The precision instrumentation, including the cone bearing in the grating turntable and the slits, was fabricated in the Physics Instrument Shop of the University of Michigan, the slits being of the Roemer and Oetjen[10] design. A precision circle ruled with a minimum angular spacing of 5 min of arc at the National Bureau of Standards is mounted on the turntable. This circle is not used for wavelength determinations but to provide a permanent calibration for all grating settings. Rotation of the grating table is provided by a worm and worm gear, also obtained from the University of Michigan, and driven by a synchronous motor through a gear box with a selection of four forward speeds and one reverse. While this does not provide the ultimate in precision of motion of rotation, it is noted that wavelength determinations are made by use of a comparison spectrum together with an interferometric fiducial marking system in instances where the highest wavelength accuracy is required. The spectrometer is not designed for evacuation but has an airtight housing to permit purging with dry nitrogen should it appear necessary. So far there has been no noticeable interference from atmospheric bands of H_2O or CO_2. Apparently, the relatively open character of the rotational fine structure greatly diminishes the probability of coincidences with emission lines. The described instrument, except for the grating initially acquired, was transferred to the Corona Laboratories following the construction of a duplicate instrument at the National Bureau of Standards.

In the meantime a second instrument has been built to accommodate one of the large Bausch & Lomb replica gratings made from one of the MIT master rulings. The specifications are as follows: grooves per mm 300; ruled width 254 mm; groove length 128 mm; first-order blaze, 5 μ. This grating is practically ghost-free. It has been tried out in a "bread-board" setup, but the spectrometer is still incomplete as to final design and construction. The present plan is to use two 25-cm aperture off-axis paraboloids in a design somewhat similar to one used by Herzberg at the National Research Council of Canada. By using two mirrors the off-axis angle condition may be realized for both entrance and exit slits.

Detectors and Amplifiers

The earlier period of observation of infrared atomic emission spectra, associated with the work of Paschen, undoubtedly came to an end because it had reached the point of diminishing returns in terms of available energy after relatively easily observable intense infrared spectra had been covered. A point-by-point technique was employed involving direct attachment of a thermal detector to a Thompson astatic galvanometer as improved by Paschen. This was long before the science of electronics had emerged and with it the development of amplifying systems. Furthermore, the thermopiles or bolometers of that period had time constants much too large to permit the use of ac amplification so successfully employed in the modern period. Actually, the first photoconductive detector had been invented and tested many years before an electronic amplifying system was developed. This was the Case[11] cell mentioned in the presentation at the Rydberg Centennial Conference.[3]

Photoconductive detectors were rediscovered at the close of World War II, but their widespread utilization in research programs was delayed for several years. Probably the first open presentation of the properties of these detectors was by Cashman[12] at the 1946 Winter Meeting of the Optical Society of America. In that period previous to establishment of large-scale manufacturing facilities, detectors could be obtained only from individuals conducting small research programs. Cashman was largely responsible for developing the art of fabricating lead sulfide detectors and for supplying them where the need was most urgent.

Covering the characteristics of various classes of detectors currently in use, an excellent introduction is the recent paper by Potter and Eisenman[13] which references an extensive literature. The whole subject of measurement of infrared radiant energy is ably covered in a recent book by Smith *et al.*[14]

Except for the work on the hydrogen spectrum,[1] all observations on atomic emission spectra have made use of lead sulfide detectors. A selected evaporated-layer, or capsule-type, cell was used until comparatively recently. Within the past two years utilization of dewar-type coolable chemically deposited cells have permitted extension of the observations as far as 40,000 Å.

It would be incorrect to assume that the properties of the lead sulfide cell limit the exploration of spectra beyond 4 μ. The emphasis on lead sulfide arises from its relatively high responsivity and the probability that most of the energy associated with infrared atomic

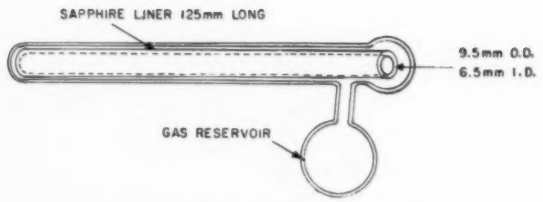

Fig. 1. Source tube with sapphire liner.

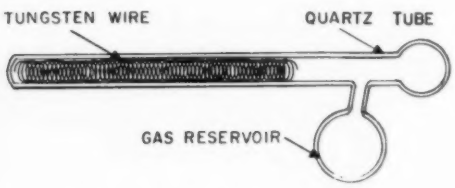

Fig. 2. Source tube with metal coil.

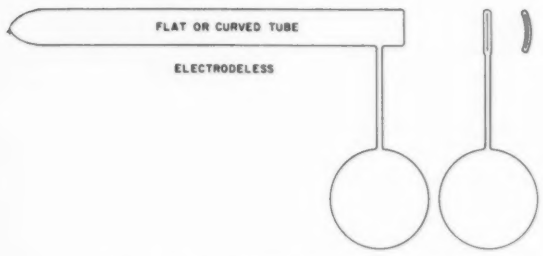

Fig. 3. Source tube with flat cavity.

spectra is bracketed within its range. Other detectors mentioned in the references[13,14] will permit extending the observations where possible. The other lead-salt detectors, lead selenide and lead telluride, are sensitive to 6 μ or more depending on the fabrication process. The semiconductor, InSb, cuts off a little beyond 5 μ. For extended observations beyond these limits other semiconductors are recommended, particularly germanium doped with traces of various metallic impurities.

Successful use of photoconductive elements in a great variety of radiometric and spectrometric applications has led to development of a considerable number of successful amplifying systems employing the ac principle. In general the radiant energy is modulated by a sectored disk or "chopper" at a rate compatible with the time constant of the detector, which is in the range from a microsecond to one or two orders of magnitude longer. For most of the work performed with the equipment described in this paper an amplifier designed by Wilson has been used.[15] This amplifier, currently tuned to a modulation frequency of 1080 cps, is capable of operation at an extremely narrow bandpass, desirable for noise elimination as small as 0.01 cps. This is accomplished by use of the inverse feedback principle. For best results, owing to the very narrow bandpass, the light "chopper" should be operated from a power supply with a precisely controlled frequency. Such devices embodying a tuning fork are available commercially. Another type of amplifier now commercially available in several designs uses the principle of synchronous rectification or phase sensitivity. A synchronizing signal, whose phase relationship to the information channel may be adjusted, is used to gate a detection or modulation stage. The synchronizing signal may be generated optically, mechanically, or electrically. A number of circuits have been designed to utilize this synchronous detection feature. The synchronous detector has two principal advantages. It makes possible the use of fairly broad band amplifiers so that a single instrument may be tuned automatically to any modulation frequency used within a fairly wide range of frequencies. This property makes the circuit essentially an automatic frequency control system which permits the use of extremely narrow bandwidths without using a carefully controlled frequency power source. The second advantage is the availability of a wide range of bandwidths by the adjustment of the time constant of the R-C filter in the rectified output of the synchronous detector. One of the early designs was described by Golay.[16] Another of several phase-sensitive circuits known to the authors is that described by Smith *et al.*[14]

The output of the amplifier may be fed into any of a number of commercially available recorders, either of the potentiometer or galvanometer type. A synchronous drive to ensure uniform chart advance is important for accurate wavelength reduction just as it is for the moving element of the spectrometer.

Sources for Excitation of Infrared Atomic Spectra

The choice of sources for use in the observing programs under consideration is somewhat more restricted than that permitted for photographic observation. Characteristics of the amplifying system require a quiet, steady source, eliminating all disruptive sparks, and generally imposing a requirement that an arc be operated in a chamber at a reduced pressure or in an inert circulating atmosphere. A helium atmosphere surrounding an enclosed arc was used to excite the previously unknown $d^{2}\text{-}^{3}F$ levels of Ca I.[17] Direct current arcs between cored carbons in air operate quietly but the CN emission bands completely dominate the spectrum out to about 1.6 μ. The choice is finally reduced to various forms of tubular sources. The Geissler tube is excellent in instances where the physical characteristics of the source element make its use possible. Noble gases lend themselves admirably to such use. From energy considerations a design permitting end-on orientation toward the spectrometer slit

is preferable particularly in circumstances where the levels involved in the observed transitions are high enough that self-reversal is not a serious problem.

A class of sources that operates well may be described as enclosed ac arcs, of which the commercially available Osram lamps provide a good example. Lamps of similar but more specialized design, as described by Marden *et al.*,[18] have been made by Beese. These operate directly from 220-V ac terminals with resistance ballast sufficient to hold the current to about 5 A, and require some sort of starting device such as a Tesla coil. These lamps have two principal handicaps: (1) Source materials are limited to permanent gases and relatively volatile elements, and (2) the enclosures, in some instances a double-wall construction, cut off the energy effectively at about 2.5 μ.

The hollow cathode source, generally associated with the name of Schüler, is in a sense a modified form of Geissler tube operated from a dc power supply at a potential of about 1 kV and drawing currents up to several hundred milliamperes. It requires a circulating gas whose ionization potential determines the level of excitation. At present argon is generally used for this purpose. Many modifications have been devised including cooling of the cathode to improve line sharpness. The source has the advantage that it can be employed with almost any solid source element. It has not, however, been too successful for infrared observations because of deficient output of energy in the extra-photographic region, in spite of extremely copious visible emission. This disappointing feature was noted particularly by Fisher who designed special cathodes having high-current capacity for infrared use.

The most successful source for radiometric observation of infrared atomic spectra is the microwave-excited electrodeless tube. A practical unit for operating this source is the Raytheon Microtherm, a 2450 Mc/sec magnetron oscillator originally designed for diathermy. The source tube may be used for gaseous elements or for solids if the latter can be volatilized under the action of the microwave energy supplied by the exciter. The problem of exciting spectra of refractory elements led Corliss *et al.*[19] to develop a technique of filling the source tubes with a relatively volatile halogen salt of the element under study. The material may be introduced as the chemical compound or prepared *in situ* by treating the element with the halogen during the filling process. In most instances, a carrier gas, usually one of the noble atmospheric gases, is necessary. The carrier gas necessarily contributes its own spectrum to an extent dependent on the relative ease of excitation of the various elements in the source. The presence of the halogen of course involves the problem of sorting out its spectrum from that of the element. Fortunately, the infrared spectra of chlorine[20] and iodine[21] are now fairly well known, and that of bromine has been observed by Tech and Corliss as far as 13,000 Å.[22] For more certain identification source fillings of different halides may be used. In the course of the authors' program and in order to realize certain special objectives several modifications of the design of the microwave-excited source, which in its simplest form is a straight section of silica or Vycor tubing sealed at the ends, have been made as follows:

(a) In order to minimize cleanup of the carrier gas and, thereby, prolong the useful life of the sources a side bulb of considerably larger capacity than the section from which the radiation is taken has been connected through a length of capillary tubing.

(b) In tubes designed for end-on use an inblown bubble window, blown extremely thin, has been formed at one end. Such a window is transparent to well beyond 4 μ, avoids the contamination from sealing on a sapphire window and permits adequate outgassing. Another advantage of the inblown construction is that the point at the center of the window is hotter than surrounding areas and is kept clean by the discharge.

(c) Tubes have been fabricated with a sapphire liner in the form of tubing telescoped loosely into the outer envelope. This modification is intended as a chemical shield to prevent interaction of the source material with the tube walls to form inert glass-like compounds. This design has been found useful with alkaline earths, calcium, and strontium. Figure 1 is a sketch of the sapphire-lined tube

(d) In order to provide internal heating and make unnecessary the use of a flame or furnace for volatilization of the source material a spiral of tungsten wire has been inserted into the tube. This spiral heated inductively by the microwave source effectively raises the temperature of the source element. This feature is shown in Fig. 2. Use of the spiral heater was found most effective in the investigation of the ytterbium. It was possible to bring the temperature of the metal inserted as the pure element up to the point where it could be excited without resorting to the formation of halogen compounds.

(e) Finally tubes have been fabricated with a flat interior section or contrasted with the usual cylindrical form. A special technique has been devised by which silica tubing is flattened against an inserted tungsten ribbon that is later withdrawn by using an acid treatment. This design, illustrated in Fig. 3, permits projection of a line-shaped image and, therefore, increased efficiency of slit illumination.

Some investigators, notably Bovey and Wise,[23] have made successful use of a cavity oscillator replacing the usual antenna of the microwave generator. A similar device has had limited use by the authors.

Although not yet employed by the authors the utilization of the gaseous maser as a source of intense infrared energy should not be overlooked. This applies

particularly to mixtures of the noble gases as demonstrated by Faust *et al.*[24] Apparently, the possibilities of the maser source have only begun to be realized.

Experimental Procedures and Data Reduction

The separation of spectral orders has in all instances been accomplished by use of optical filters. An adequate array of materials is now available and a choice of the filter method over use of a foreprism permits considerable simplification of equipment. For use with a 600 lines/mm grating for exploring the 1-μ to 3-μ region, three long-wave pass filters are usually adequate: a Corning glass described by code number 2540 with transmission rising from incidence at about 8000 Å, reaching a peak near 9000 Å, and showing typical glass transmittance to about 2.7 μ; a silicon polished section, with incident transmission at 1.05 μ, reading a fairly level plateau at 1.1 μ; and a germanium section with corresponding wavelengths for incidence and plateau, 1.5 and 1.8 μ. The semiconductor filters are more transparent if coated for appropriate regions. For both, the upper limit is somewhat vague but beyond the limits of the described experiments. Use of a 300 line/mm grating, because of the crowding of orders, requires somewhat more sophisticated filters of narrower bandpass. Development of the art of optical coating has made such filters available for any selected region within the grating range.

Data reduction for determination of wavelengths are, in these experiments, always accomplished by introduction of a comparison spectrum rather than by utilization of the geometric properties of the grating. Owing to the availability of only one channel including the photoconductive detector and amplifying system, the comparison spectrum is introduced along with the source energy under study and over the same optical path, something that is desirable in any event to avoid possible displacements on the record. In many instances the comparison spectrum is generated within the experimental source either from a carrier gas, usually argon, or a halogen used in the manner described. Various devices for introducing radiant energy from an independent source have been described. One of these is described and illustrated in the paper by one of the authors on Ca I.[17] The illustration is reproduced here as Fig. 4 and the arrangement of components is fairly obvious. A real image of the experimental source is formed by a concave spherical mirror at the central point of a vertically mounted tubular noble gas source, this point being at the common focus of the mirror and a projecting lens. The comparison source may be removed or inserted from the path during the scan according to the need for standards. This system permits the use of higher order standards but the primary source may be filtered as desired. Another arrangement described in one of our internal reports[25] achieves essentially the same objective but is intended to accommodate simultaneous use of two electrodeless sources and microwave oscillators. This system is illustrated by Fig. 5. In this instance the filter, as for example a silicon plate, serves also as a reflector to bring the radiant energy of the comparison source into the optical path.

Wavelength reduction from the chart recordings has been accomplished by a simple linear interpolation between lines of the spectrum under study and the comparison source. Wavelengths of first-order standards are compiled and discussed in several internal reports by the authors.[26] A relatively simple computer program has been developed to accomplish the reduction. The reduction procedures must be modified where the angle of incidence at the grating is large enough that nonlinearity of dispersion is significant. These procedures involving use of correction curves are equivalent to those used in reducing photographic spectrograms. In early experiments a system of fiducial marks was placed upon the chart by permitting a microswitch to engage one of the gear elements. This was subsequently found to be no more precise than use of the rectangular grid printed on the chart paper. This whole procedure is obviously open to criticism because of non-uniformity in the grating drive and impossibility of always having a favorable distribution of standards.

Consequently, in recent experiments we have made use of a system of interferometric fiducial marking in which the fringes formed by a Fabry-Perot interferometer illuminated by a source of continuous radiation, and picked up by a photomultiplier through a separate channel, are displayed alongside the spectrum by a dual

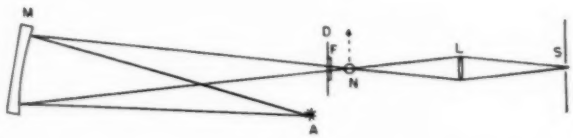

Fig. 4. Arrangement for projecting image of source upon slit of spectrometer. A—arc lamp; N—neon tube; M—concave mirror; D—diaphragm with horizontal slot; F—filter; L—quartz lens; S—spectrometer slit.

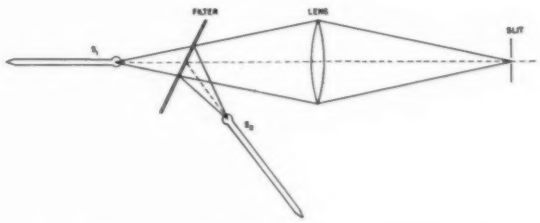

Fig. 5. Arrangement for introduction of comparison spectrum by reflection from filter surface.

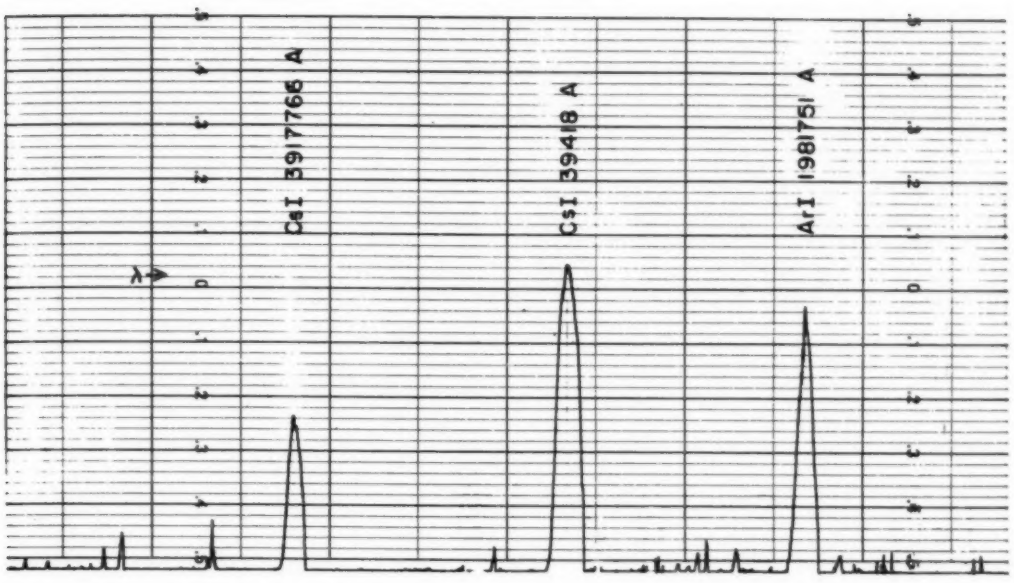

Fig. 6. Section of chart record of Cs I with second-order Ar I comparison.

recorder. Actually the use of interference fringes for calibration is very old in the history of infrared spectroradiometry but its application to high resolution by Douglas, Rank, Plyler, and others is fairly recent. In all instances illumination of separate portions of the entrance slit by the continuum and experimental source leads to the formation of separate spectra at the exit slit but are switched in position vertically. Specific reference here is limited to systems designed for observation of atomic emission spectra. One of these was reported by Fisher.[27] This system differs from most of the others in that the interferometer is placed behind the exit slit instead of in front of the entrance slit. The interferometric system has several advantages, the principal one being that all fringes of a given grating order have the same separation in units of frequency. Actually then, to obtain the wavenumber of an unknown line, knowing the wavenumber separation of the fringes, it is necessary to determine only the whole number and fractional residue of fringes between the line and a standard of known wavenumber. We are thus freed of the difficulties associated with nonlinearity of dispersion and the whole reduction may be made by a linear formulation in wavenumber units. The correction for atmospheric dispersion is generally insignificant when compared with the precision of measurements of the records that are attainable. An important precaution to be exercised is to make sure, by appropriate filtering, that there is no blending of grating orders in the fringe system. It is also important to use sufficiently narrow slits that the fringes will be clearly resolved. In practice the instrumental line profile should not be wider than about half the distance between successive fringes. Of course with available photomultipliers it is necessary to use orders in the visible range. The reduction also lends itself readily to computer programming. Achievement of wavenumber precision as high as 0.02 cm^{-1} has been reported by Eriksson and Johansson[28] at the University of Lund.

III. Concluding Remarks

It is not the purpose of this paper to report data from selected spectra. A small section of record is reproduced as Fig. 6 to illustrate the possibilities of observation in the 4.0-μ region. The profiles shown, selected from a section of a record of Cs I, are described as follows:

	Å	cm^{-1}	Transition
Cs I	39,177.66	2551.779	$5p^6 7p^2 P_0{}^\circ{}_{1/2}$—$5p^6 8s^2 S_{01/2}$
Cs I	39,418	2536.2	$5p^6 4f^2 F^\circ$—$5p^6 5g^2 G$
Ar I	19,817.51	5044.666	$3p^5 3d[1^1/_2]_2^\circ$—$3p^5 5p[1^1/_2]_2$

The strongest line of this group is representative of lines of analogous classification found half a century ago by Paschen in the spectra of each of the alkalies. Since terms from peripheral configurations are nearly hydrogenic it almost coincides with the first line of the Brackett series.

It is emphasized in conclusion that it is altogether feasible to observe and describe atomic spectra at least as far as 4μ, using available detectors. Emission of energy near this upper limit appears probable for essentially all atomic spectra.

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Meeting Reports *continued from page 664*

The fact that the $^1G_4 \rightarrow {}^3H_6$ luminescence of Tm^{+3} is observed in TmB_3 but not in TmD_3 allows one to infer that the original excitation of the organic part is transferred to the rare earth via the triplet state. (Lifetimes are analyzed, using flash pumping. While Crosby and other workers in this field are not unmindful of the possible development of laser action in such systems, they have justified these studies on the basis of their intrinsic interest.) A. L. Schawlow *Stanford University* recounted the development of the maser and its relatives at other wavelengths, with stimulating anecdotes concerning his association with C. H. Townes during the development of the idea of the possibility of infrared and visible masers and with much acronymology pertaining to newer devices. Choosing in part the theme "What Spectroscopy Can Do for Quantum Electronics and Vice Versa", Schawlow discussed maser action from ruby lines arising from adjacent pairs of Cr^{+3} in crystals with higher concentrations, the narrowing of the ruby line at lower temperatures where residual width is apparently due to strain; under favorable conditions, the linewidth approaches 2 parts in 10^7 of the frequency. (A brief account was also given of photochemical studies of Br_2, using maser sources in which individual rotational lines can be excited and possible separation of the 79 and 81 isotopes achieved.)

The second session, "Solid State", was only in a limited sense more concerned with solids than was the first session, in which all the laser materials discussed were solids. J. C. Decius *Oregon State University* spoke on "Vibrational Spectroscopy of Small Molecules in Crystals and Crystalline Solid Solutions", with emphasis upon the quantitative information bearing upon intermolecular forces which can be gleaned from such work. (Evidence for the formation of ion pairs $^{++}MSO_4{}^{--}$ with M = Ca, Ba, Pb in single crystals of KCl and KBr was presented. If M^{++} substitutes for K^+ and $SO_4{}^{--}$ for Cl^- in the nearest neighbor positions of the alkali halide lattice, $SO_4{}^{--}$ will see C_{2v} symmetry. The observed vibrational spectrum agrees qualitatively and semiquantitatively with this model.) Rare earths made still another appearance on the program in the paper entitled "Far Infrared Spectra of Magnetic Oxides" by A. J. Sievers *Cornell University*. Magnetic resonance experiments in various solids are well known, but the transitions between various spin levels at zero applied field have only been observed in the far infrared relatively recently, usually in the range from 5 to 100 cm^{-1}—below the lowest lattice frequencies. Sievers described the results of such studies on the rare-earth iron garnet, $5Fe_2O_3 \cdot 3Yb_2O_3$. (Other rare-earth iron garnets were also discussed. Observed frequencies are strongly temperature dependent over the range from 2° to 40°K.) Presently, available resolution in this region is of the order of 100 (0.1 cm^{-1} at 10 cm^{-1}), but is adequate for the line-widths so far encountered.

The "High Resolution" session opened with D. H. Rank's account of "Shifts and Breadths of Molecular Band Lines". Professor Rank *Pennsylvania State University* obviously relishes the discomfiture of the theorists, and his work in the infrared between 2000 and 4000 cm^{-1}, in which resolution of about 0.02 cm^{-1} is achieved along with an accuracy of about 0.001 cm^{-1} in the determination of individual lines, provides several opportunities to make them squirm. For example, the HCl lines exhibit shifts of the order of $\Delta\omega = 0.1$ cm^{-1} per atm of added inert gas. Such shifts are markedly J dependent, usually red shifts (although He produces blue shifts), and generally increase with the polarizability of the added gas. (Rank also gave an account of recent investigations of quadrupole or induced dipole transitions at relatively low pressures but very high resolution.) W. Klemperer *Harvard* followed with a talk entitled "Molecular Beams". The electric-resonance spectrometer, pioneered by I. I. Rabi, has been applied by Klemperer and his associates to refractory materials such as BaO and SrO, produced at 2000°K, whose dipole moments have been evaluated in the first six vibrational quantum states with an accuracy of about 10^{-3} Debye. Other molecules reported included $^6Li^{19}F$, LiH, and LiD. Klemperer emphasized that the dipole moment of lithium hydride provides a particularly useful test of the wave functions which are these days being produced with the aid of machine calculations by the quantum-mechanical theoreticians. Many molecular constants are obtained with the very high precision characteristic of the radio-frequency region: for example, the dipole moment of $^6Li^{19}F$ is known to 10^{-5} D as a function involving both linear and quadratic terms in $(v + {}^1/_2)$.

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Spectroscopic Line-Profile Studies of Long Magnetically Confined High-Current, Steady-State Vacuum Arcs

J. R. McNally, Jr., and M. R. Skidmore

Spectroscopic studies of the line profiles of radiating ions in a magnetically confined, high-current, steady-state vacuum carbon arc have revealed ion temperatures up to 5,000,000°K in a 4.9-m long arc. The ion temperature is a quadratic function of the distance from the anode in a given arc, but for arcs of different lengths the highest arc temperature is roughly proportional to the arc length. The spectrum line profiles are essentially Gaussian (Doppler shape) for observations transverse to the arc column but in very long arcs are non-Gaussian, and sharper, for axial views. Helium, nitrogen, or argon fed to the arc through the cathode result in pronounced heating of the trapped ions, their transverse temperature being dependent on the charge state of the ion, thus suggesting strong radial electric field heating of the ions.

I. Review of Early Experiments on Hot Arcs in Magnetic Fields

In 1955 unusual spectral line shapes were observed for ionic spectrum lines from a calutron arc in a magnetic field (PIG discharge). The ionic lines were broader than the neutral lines and, in addition, showed a slant line appearance somewhat like spectral shifts observed for rapidly rotating stellar bodies. These phenomena were first reported in 1956[1] and reviewed in 1959.[2] The line slants were attributed to cooperative effects in the arcs arising from strong radial electric fields of about 100 V/cm, i.e., the slant lines resulted from an $E_r \times H$ counter-Larmor precessional drift about the arc axis. Subsequent experiments showed the slant effect to be magnetic field dependent, the azimuthal drift velocity increasing almost linearly with applied magnetic field.[3]

Thermonuclear type experiments at ORNL led to the development of the Luce carbon arc,[4] which immediately received spectroscopic attention. Slant and line broadenings were especially pronounced in this high-current (~150 A), magnetically confined, steady-state vacuum arc. Figure 1 is a reproduction of a spectrogram showing axial and transverse views of the arc taken with a Bausch & Lomb echelle spectrograph in a stigmatic optical arrangement. The rotation of ions in the arc column is indicated by the slant Doppler shift in the transverse view. The line broadening of carbon lines in both axial and transverse views may be compared with that of the sharp mercury reference line. Skidmore *et al.*[5] reported on ion temperatures up to 500,000°K in the Luce arc in 1959. In 1960 ion temperatures up to 800,000°K and electron temperatures generally less than 60,000°K were reported.[6] A comprehensive survey of carbon arc spectroscopic studies was also given in 1960.[7] The basic properties of the Luce carbon arc as of that date included electron density of 10^{14} electrons/cm^3, electron temperature ~40,000°K, ion temperatures to 800,000°K, and axial and radial ion drift velocities up to 10^6 cm/sec. A review of ion energy evaluation procedures was presented in 1961 by Griffin *et al.*[8]

One of the most unusual features noted of the magnetically confined carbon arc was the quadratic increase of the transverse ion temperature with the distance of the observation point from the anode electrode, i.e., $T \alpha l$.[2] This has led to a new series of experimental studies which form the basis of the present paper. The inter-ionic Stark field of less than 1000 V/cm for ion densities of 3×10^{13} ions/cm^3 should introduce negligible Stark broadening except for levels of very high-quantum number.

II. Preliminary Studies

A brief study was made with a Jarrell-Ash Ebert 82,000 spectrometer of a long (214 cm) carbon arc in a 305-cm solenoid. The first experiment involved the use of a 10-cm o.d. carbon anode and 13-mm tapered tungsten cathode at magnetic fields of 7.5 to 9 kG.

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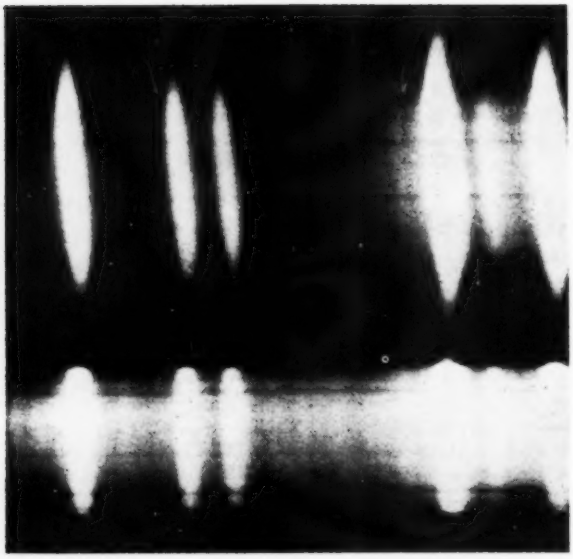

Fig. 1. Doppler slant and broadening in C III spectra at λ 4650 Å as viewed both transverse and parallel to arc using a Bausch & Lomb echelle spectrograph (slant lines represent transverse view).

Arc current was 115 A and the arc voltage varied from 220–240 V. Outgassing was serious, and the lowest pressure was 7×10^{-5} torr. Without polarization separation the line-width at half intensity as observed at a point 183 cm from the anode was only 0.52 Å. Subsequent runs (using a 5-cm o.d. carbon anode and a 16-mm tapered tungsten cathode, no polarizer, and very short 5-μ wide slits which reduced the instrument half-width from 0.3 to 0.2 Å) gave half-widths ranging from 0.4 to 0.5 Å with an average of 0.43 Å. The half-width, corrected for instrumental broadening, was 0.39 Å and corresponds to a C III ion temperature of about 150,000°K. Pressure was still high (4×10^{-5} torr at the midpoint of the solenoid) and may account in part for this relatively low ion temperature.

The use of carbon for both electrodes gave much higher ion temperatures. A 13-mm o.d. carbon cathode with a 1.6-mm hole for starting with argon gas feed was used. Results of the first run are given in Fig. 2 and show a time-dependent effect of both the half-width (full width at half-intensity), $\Delta\lambda_{1/2}$ of the 4647 C III line and the mid-solenoid pressure. The highest ion temperature attained was about 1,400,000°K. A π-transmitting optical polarizer reduced temperature corrections due to Zeeman contributions to about 3%; the slit correction is estimated to be 7% at 1,400,000°K.

The increase in spectral line-width with distance from the anode is illustrated in Fig. 3. A slight slant effect (due to Doppler shifts introduced by precessional motion of the ions about the arc axis) is discernible in the figure (compare 12th order, 4650-Å line with 22nd order, 2537 Å of Hg in bottom spectrum). The hollowness of the arc, in regard to C III radiation, also appears to increase with distance from the anode. This may be due in part to the radial distribution of C III ions shifting outward for ions farther away from the anode or, more likely, to the improved definition of the electron streamers leaving the outer edges of the cathode. The Larmor diameter of doubly ionized carbon ions having a mean energy of 120 eV and in a field of 8265 G is 0.63 cm, a figure comparable to the radius of the carbon arc. This suggests that the hollowness may be due mostly to a hollow spatial distribution of the electron streams from the cathode. The streamers may also play a major role in the ion heating processes, since no arc without streamers has as yet produced such high temperatures.

The Gaussian nature of the 4647-Å line profile was checked in two simple ways. The first method consisted of plotting the observed relative intensity vs $\Delta\lambda/\Delta\lambda_{1/2}$, normalizing to a maximum intensity of unity (see Fig. 4). The Doppler half-width, $\Delta\lambda_{1/2}$, was evaluated at the half-intensity point and the theoretical Doppler curve (solid curve)

$$I = I_0 \exp[-\ln 2(\Delta\lambda/\Delta\lambda_{1/2})^2]$$

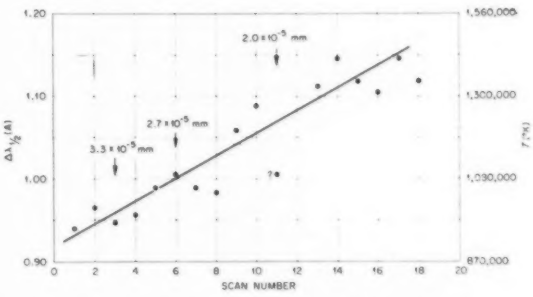

Fig. 2. Time-dependence of Doppler half-width and ion temperature during early stages of arc operation [time interval approximately 2 min/scan]. Carbon arc, 7700 G, 183 cm from anode, 218-cm arc length, 177 Å, 142 V.

drawn for comparison. For this case, $\Delta\lambda_{1/2} = 1.10$ Å ($T = 1{,}300{,}000$°K) and $I_0 = 1.0$ define the Gaussian. This method utilizes only three points of the observed profile and is very sensitive to the choice of I_0.

A second easy method of verifying the Gaussian nature of line profiles was used in which the log of the relative intensity is plotted against $(\Delta\lambda)^2$ (see Fig. 5). The intercept of the fitted straight line for $(\Delta\lambda)^2 = 0$ is log I_0 and the slope of the line determined $\Delta\lambda_{1/2}$ to be 1.155 Å ($T = 1{,}430{,}000$°K) in this example. The straightness of the fit demonstrates that the profile is Gaussian down to about 5% of the peak intensity. A rough check of the C II line at 4267 Å at the same high pressure gave the same line half-width within 10% of the C III 4647-Å line (but see Sec. IV)

Figure 6 shows the dependence on magnetic field of the half-width and the ion temperature. Arc voltage increased monotonically with magnetic field increase. For 5500 G and for 15,100 G there was considerable arc flutter; precision, as shown, is much worse than for intermediate fields.

These preliminary studies in the 305-cm solenoid showed that still higher temperatures could be attained than previously reported and that a Doppler profile fitted the experimental line-intensity data for these observations transverse to the arc axis.

III. Higher Steady-State Ion Temperatures in Longer, Low-Pressure Carbon Arcs

Doppler studies continued in the 305-cm long solenoid utilizing various observation ports (20 cm apart), a magnetic field (usually 8200 G) uniform to within 5% on axis[9] and lower operating pressures Results indicated a continued rapid increase of ion temperature with distance from the anode. Figure 7 shows spectrograms of the 4650 C III triplet taken 20 and 203 cm from the anode using a JACO 3.4-m spectrograph at a grating angle of 55°. For the 203-cm case the 4650- and 4651-Å lines show no intensity minimum between them and the 4647-Å line-width is comparable to the interval between it and the 4650-Å line. The Doppler "slant" spectrum line effect due to azimuthal rotation of ions about the arc axis in a radial, negative potential well is still pronounced in the regions near the anode but is not obvious in the cathode region because of the very wide Doppler broadening.

The usual bright filamentary structure or streamer character of the arc is observed along the whole length of arc and apparently originates in cathode hot spots (usually about 4–8 filaments may be observed). These streamers may be related to the early streamer work of Cummings and Tonks,[10] which was done at 4 A in fields less than 100 G, but at high neutral gas densities of mercury vapor. Exposure times for most spectrograms averaged out the streamer distributions.

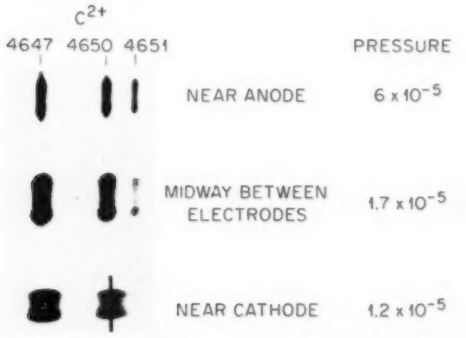

Fig. 3. Variation of Doppler line-width with distance from anode in a long carbon arc (transverse observations) as obtained with 3.4-m JACO Ebert spectrograph. Arc current: 192 A; arc voltage: 140 V; field: 8265 G.

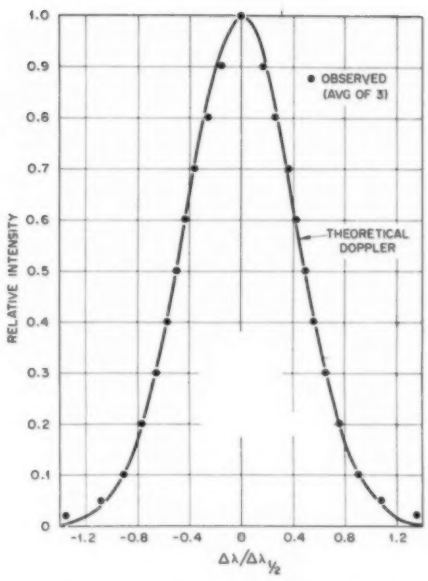

Fig. 4. Observed line profile vs Doppler profile for 1,300,000 °K C III line at λ 4647 Å. Carbon arc: 180 A, 142 V, 183 cm from anode, 218-cm arc length.

Scanning of the C III triplet at 5 Å/min (using a JAco-82,000, 50-cm spectrometer) gave adequate data for line-profile studies of the 4647-Å line and evaluation of ion temperatures.[11] A π-transmitting Glan polarizer was used to reduce Zeeman structure contributions to the line broadening to less than 3%. A magnetic field strength of about 8000 G gave steady operation of the arc between a 5-cm diam carbon anode and a 13-mm o.d., 9.5-mm i.d. carbon cathode at an arc current of about 140 A and voltage of about 150 V.

Temperature evaluations and data handling for numerous cases were done on the ORACLE using a Linear Regressions and Correlation Code.[12] This code gives a linear least-squares fit to the curve of log I vs $(\Delta\lambda)^2$, as shown in Fig. 8, the slope of which determines the best value of the half-width of the line. The spectrum line profiles were in all cases Gaussian (down to about 15% for $T \sim 2.5 \times 10^6$ °K where overlap with 4650 began), as indicated by the linearity of the curve. The line slope corresponded to half-widths generally in excess of 1.5 Å ($T_{C\,III} = 2.5 \times 10^6$ °K at the lowest operating pressures ($\sim 2 \times 10^{-6}$ torr). The reduction in base pressure by a factor of about five over the preliminary data (see previous section) resulted in approximately doubling the ion temperature. It is probable that the lower arc current also contributed to this temperature increase (see ref. 8). The instrumental broadening correction of 0.3 Å at 4650 Å reduces the observed temperature by about 100,000°K at 2.66×10^6°K.

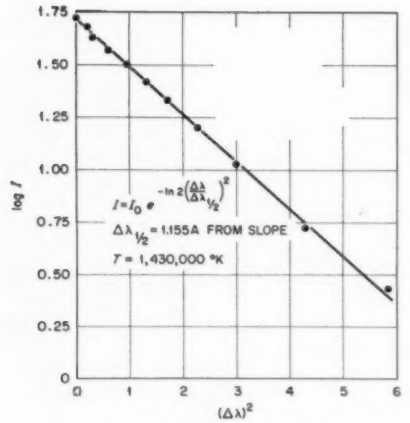

Fig. 5. Evaluation of half-width and ion temperature from best-fitting Gaussian. Carbon arc: 7700 G, 180 A, 145 V, 183 cm from anode, 218-cm arc length, 1.1×10^{-5} torr.

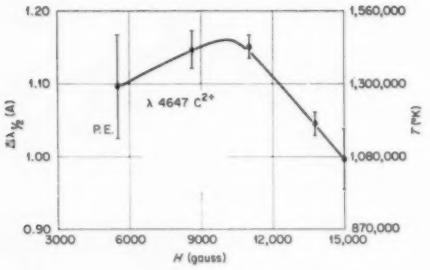

Fig. 6. Dependence of Doppler half-width and ion temperature on magnetic field. Lower arc voltage at low field. 183 cm from anode, 218-cm arc length, 188 A, 129–152 V, 12×10^{-5} torr.

In a 224-cm long arc and at a distance of 203 cm from the anode $T_{C\,III}$ was determined to be (uncorrected for instrumental width) 2.7×10^6°K from another series of measurements at low pressure, using half-widths only, in which $T_{C\,II}$ from λ 2512 Å was evaluated as 3.0×10^6°K, and $T_{C\,IV}$ from λ 2529 Å was 3.3×10^6°K. Instrumental width corrections are −100,000°K, −330,000°K, and −370,000°K, respectively. Detailed line profile studies of λ 2512 Å and λ 2529 Å were not made because of their low intensity; also, no corrections were made for their fine structure or σ components.

IV. Very High Steady-State Temperatures in Very Long Carbon Arcs

More recently, Doppler studies have been made of a 493-cm carbon arc, obtained by adding the old solenoid facility[13] to the 305-cm solenoid.[9] Observations, made transverse to the arc axis, gave carbon ion temperatures up to 5×10^6 °K at a point 452 cm from the anode. Instrumental half-width was 0.2 Å in this series of measurements, and a Glan prism was used to transmit the π polarization. The quadratic increase of the ion temperature with anode distance is illustrated in Fig. 9, the extrapolated portion at small half-widths (lower dashed line) agreeing approximately with the slope of the earlier studies.[8] The slope of the curve from the first point on is definitely less than that previously observed for the shorter arc and different magnetic geometry. The maximum temperature in the figure is 4.1×10^6 °K.

The quadratic increase in ion temperature with anode distance as shown in Fig. 9 is characteristic only of a given arc and cannot be extrapolated to arcs of different lengths. Thus, the highest ion temperatures observed for 137- 244-, and 493-cm carbon arcs were about 900,000, 2,500,000, and 5,000,000°K—roughly a linear dependence.

Overlap of λ 4647 Å with λ 4650 Å in the C III blue triplet introduces a 7% overestimate of the half-width at $\Delta\lambda_{1/2} \cong 2.0$ Å (Fig. 10). As a further check on the ion temperature, the C III singlet transition at λ 2296 Å was evaluated and gave transverse ion temperatures for the π component also ranging from 4 to 5 million °K—the line profile was Gaussian down to less than 10% of the peak intensity.

Observations of λ 4647 Å near the cathode, using a Stellite mirror to view the arc nearly axially (about 6° off-axis and looking in the direction of the cathode end of the system), gave line half-widths of 0.9–1.0 Å (approximately 10^6 °K), whereas the transverse views gave 2 Å (4.5×10^6 °K) (see Fig. 11). The line profile for the axial view was, in addition, non-Gaussian, having high-energy tails greater in intensity than to be

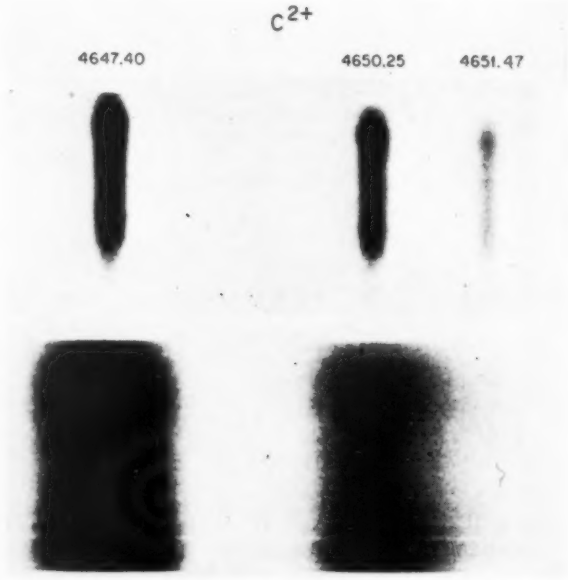

Fig. 7. Spectrogram of C III λ 4650 Å triplet showing relative line broadening near anode and 203 cm from anode (broad lines) in 224-cm long carbon arc.

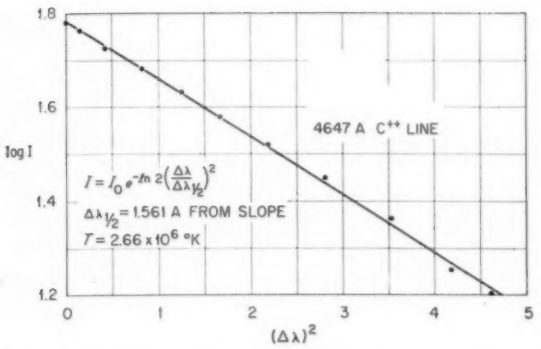
4647 A C++ LINE
log I
$I = I_0 e^{-\ln 2\left(\frac{\Delta\lambda}{\Delta\lambda_{1/2}}\right)^2}$
$\Delta\lambda_{1/2}$ = 1.561 A FROM SLOPE
$T = 2.66 \times 10^6$ °K
$(\Delta\lambda)^2$

Fig. 8. Evaluation of best-fitting Gaussian to data points obtained from a 254-cm long carbon arc; view 244 cm from anode, 130 A, 135 V, 2×10^{-6} torr, 8300 Ge.

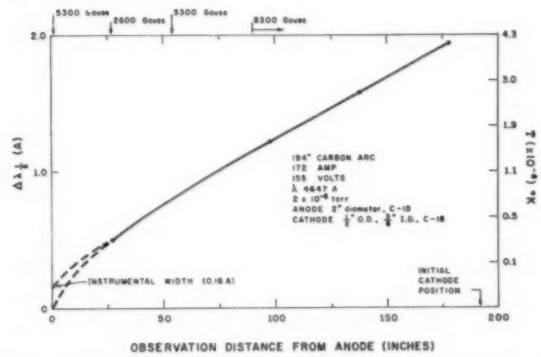

Fig. 9. Observed line half-widths and ion temperatures for four observation ports (transverse views) along a 493 cm long carbon arc. Magnetic field at various points along arc indicated at top left of figure. Arc: 172 A, 155 V, tank pressure 2×10^{-6} torr. Anode: 5-cm diam, C-18; Cathode: 13-mm o.d., 9.5-mm i.d., C-18.

expected for a half-width of 1 Å. In addition, the tail toward longer wavelength was somewhat more intense, indicating a net, small ion drift of fast ions toward the cathode. Thus, most of the ions seen axially are relatively cooler than those seen transversely but do have a high-energy group present as though collisions are converting transverse momentum to axial momentum. This is evidence that a true temperature does not exist in this region of the carbon arc and is also in keeping with the longer mean free path expected for the scattering of energetic ions along flux lines to other portions of the arc (the mean free path for 90° multiple small-angle scattering of doubly charged carbon ions at $T = 5 \times 10^6$ °K is approximately 40 m, whereas for 1×10^6 °K it is still approximately 1.7 m). Randomization and heating in this very long arc apparently occurs in two directions (r, θ), but, because of the long-scattering mean free path, scattering into the z direction results in loss of ions to other points along the arc or to the electrodes. Thus, it is probably more meaningful to describe the temperature as a "kinetic" or two-dimensional temperature near the cathode in long arcs; that is to say

$$\bar{E} \cong 5 \times 10^6/11{,}600 = 430 \text{ eV}.$$

V. Electrode Feed

The consumption of 27.9 g of anode material over a 9-hr, 21-min total run time for one carbon anode in a 4.9-m arc indicates a positive ion current of about 7 $\times Z_{\text{eff}}$ A (21 A if $Z_{\text{eff}} = 3$ or of order 15% positive ion current). This assumes negligible neutral material loss from the anode, and no return flux. The anode burns away primarily along magnetic flux lines intercepting the cathode face, frequently leaving a carbon peak (13 to 19 mm high) in the anode at the arc center. Considerable cathode erosion also feeds carbon ions and electrons into the arc column. In view of the large Larmor radii for these energetic positive ions and the requirement for quasi-electrical neutrality, this suggests that most of the electron current is associated with runaway electron streams originating from near the annular face of the cathode. These streams are very well defined in the cathode region and spread out to only a few mm diameter in the anode region of very long arcs.

VI. Fuel Ion Heating Analogy in the Magnetically Confined, Steady-State Carbon Arc

It is of both thermonuclear and spectroscopic interest to evaluate the heating of impurity gas fed as "fuel material" to these steady-state arc plasmas in order to ascertain the degree of heating and equilibration attainable between "fuel" and carbon ions. Our first experiments, using a 244-cm long arc for which ion temperatures up to 2.7×10^6 °K have been observed, gave negative results for hydrogen gas leaked into either the carbon anode or cathode. This result apparently stems from the indirect method available for observation of the heating of hydrogen ions, namely, the hydrogen ions must undergo a recombination process before radiating spectra. The probability of recombination to the nth quantum level is of order $1/n^3$ so that only about 1% of these can produce H_β quanta (λ 4861 Å) which must then compete with radiation from excited cool

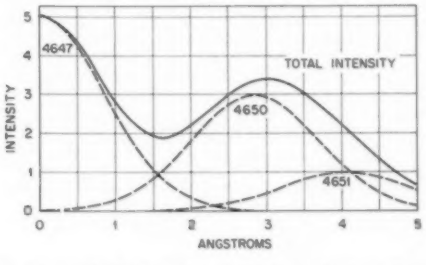

Fig. 10. Theoretical line shape for Doppler-broadened C III triplet to evaluate errors in half-width determination at very high ion temperatures. T = 4,300,000 °K.

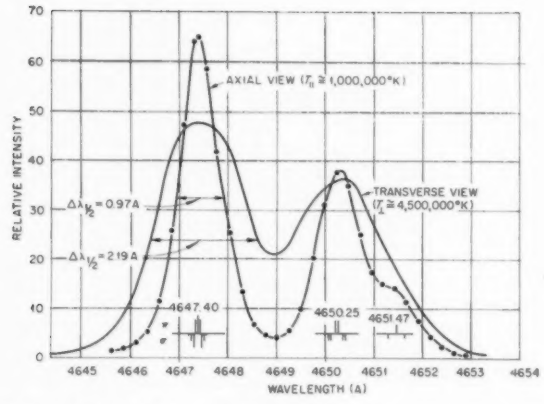

Fig. 11. Observed line profiles for axial and transverse view in 493-cm long carbon arc. Zeeman components shown in lower portion of figure (axial view sees the σ components, transverse view with polarizer sees π components).

neutrals. The observed H_β line-widths corresponded to less than 40,000°K, which is comparable to the kinetic energy of molecular dissociation fragments. It was concluded that spectroscopic observation of heating of hydrogen (or heavy hydrogen fusion fuel) does not appear feasible in this arc.

Helium was next studied since the He II trapped in the arc can be directly excited by electrons. The 4 to 3 transition at λ 4686 Å was investigated with our 50-cm JACO-Ebert spectrometer. Gas feed ($\gtrsim 3$ cm^3/min) to anode, cathode, or the vacuum tank directly revealed marked broadening of the He II line but cathode feed permitted arc operation at the lowest tank pressure. Observation point was 224 cm from the anode in a 244-cm long arc. The half-widths ranged from 1.25 to 1.68 Å for He II while the λ 4647 Å line of C III varied from 1.05 to 1.38 Å, the largest half-widths being obtained at the lowest tank pressures. These line-widths correspond to ion temperatures of approximately 0.6×10^6 °K, 1.0×10^6 °K, 1.2×10^6 °K, and 2.0×10^6 °K, respectively, indicating that the He II ion is heated to a temperature of 50% of the C III ions. Figure 12 shows the closeness of fit of the observed intensity points for λ 4686 Å to a Doppler (Gaussian) profile, indicating that it may be meaningful to ascribe a transverse temperature to these ions. The fine structure intensities shown were evaluated by the method of Bates and Damgaard.[14]

Studies of nitrogen and argon fed carbon arcs showed that ion heating is markedly dependent on the charge state of the ion. Ion temperatures, evaluated from line half-widths corrected for instrumental broadening, vary with gas feed but, for the 244-cm arc, are of order 1.5×10^6 °K (N II), 2.5×10^6 °K (N III), 2.5×10^6 °K (N IV), 1.4×10^6 °K (Ar II), and 2.6×10^6 °K (Ar III) whereas the carbon ion temperatures are 2.0×10^6 °K (C II) and 2.5×10^6 °K (C III). This strong dependence of ion heating on charge state suggests that the heating mechanism is probably electrostatic in origin. In addition, Fig. 11 shows that heating is more pronounced transverse to the arc than parallel to the arc axis indicating that the electric fields are primarily radial. A large radial electric field is in agreement with probe experiments.[13] The closer match of the two carbon ion temperatures is probably due to resonance charge transfer processes among the high-density carbon ions which cause these ions to lose more rapidly their specific charge identity. The line profiles for N II and N IV are given in Figs. 13 and 14, the former suggesting some additional heating of N II ions in the line wings due possibly to partial equilibration. The N IV ion temperature appears to be somewhat low based on this model of electrostatic heating but the radiation may possibly proceed from simultaneous ionization and excitation of the doubly ionized specie (N II) and hence

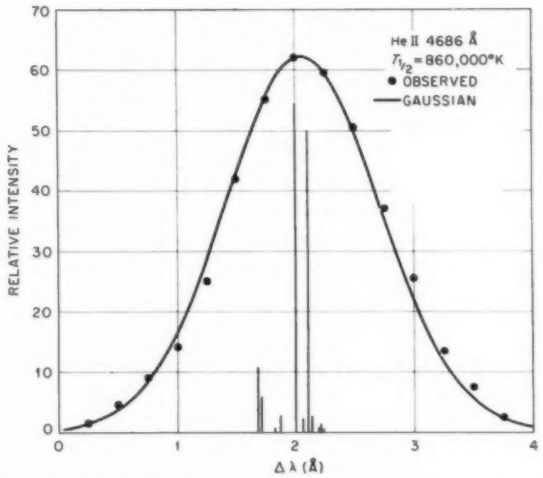

Fig. 12. Observed line profile of λ 4686 Å He II line, fitted Gaussian, and theoretical fine structure. ● 244-cm carbon arc, 224 cm from anode. Cathode feed, 1.3×10^{-5} torr, 158 V, 152 A.

show heating which is more characteristic of N III. The lack of a true thermodynamic equilibrium is also evidenced by the unusually large discrepancy between the electron temperature of only about 40,000°K and ion temperatures up to 5×10^6 °K in longer arcs.

VII. Possible Implications to Fuel Feed, Heating, and Stability in a Thermonuclear System

These preliminary spectroscopic experiments on ion heating in magnetically confined plasmas suggest that cold "fuel" gas may be heated rapidly to quite high temperatures in a hot ion plasma having high transverse electric fields. The experiments, and oth-

ers,* also suggest that the carbon and fuel ions can flow readily along magnetic flux lines from the negative electrode against the axial electric field of the arc, a result which is consistent with the kinetic pressure nkT ($\sim 10^{-2}$ atm), exceeding the axial electric pressure $\xi^2/8\pi$ ($\sim 10^{-13}$ atm). Thus, the ion feed and heating observations in the long carbon arc may have important implications to the problem of feeding and heating fuel material in a steady-state thermonuclear reaction (a temperature in excess of 40 million degrees is required to ignite a pure $D \cdot T$ reaction[15]).

It is believed that the apparent stability of these long, magnetically confined arcs may be associated with the dynamic character of the system and thus may have an important relation to stability in a thermonuclear system. It seems that strong interactions or instabilities, if any, occur mainly along flux lines and may be tolerated if appropriate potential gradients, ion and electron feed (tens of amperes) and electron damping (radiative cooling) are present. Total arc power is only about 25 kW. Diffusion across magnetic field lines, according to the normal diffusion theory of electrons in a magnetic field of 8000 G, is presumably small [i.e., $1/(\omega^2 \tau^2) \cong 10^{-6}$]. The magnetic pressure $B^2/8\pi$, supporting the arc is 2.5 atm at 8000 G.

VIII. Future Research

We hope to have the 4.9-m arc facility rebuilt, or possibly extended, in order to make spectroscopic studies of carbon and feed gases at higher ion temperatures ($\geqq 5 \times 10^6$ °K). We may also examine the heating of deuterium by the study of thermonuclear fusion processes, although the anticipated reaction rate is expected to be quite low.

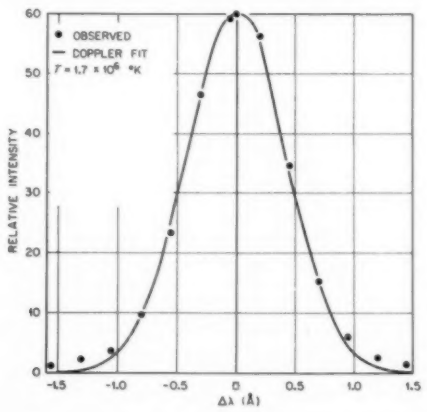

Fig. 13. Observed and fitted Gaussian profile of λ 3995 Å N II line. Note hotter "wings" of line than Gaussian fit. 244-cm carbon arc, 149 A, 128 V, 8300 G, gas feed to cathode. Tank pressure: 9×10^{-6} torr.

* For example, a lithium supplied metal anode and carbon cathode showed the characteristic green color (λ 5485 Å of Li II) extending out about 100 cm from the anode and the characteristic blue color of carbon (λ 4650-Å triplet of C III) extending out from the cathode about 100 cm. Spectroscopic observations confirmed these visual appearances.

We wish to acknowledge the contributions of H. H. Terry and B. B. Coulter, research mechanics in the Y-12 Research Services Department. We are also indebted to J. E. Francis, P. M. Jenkins, W. L. Wright, D. A. Griffin, P. M. Griffin, G. K. Werner, W. F. Peed, P. R. Bell, and E. D. Shipley for significant contributions to the work.

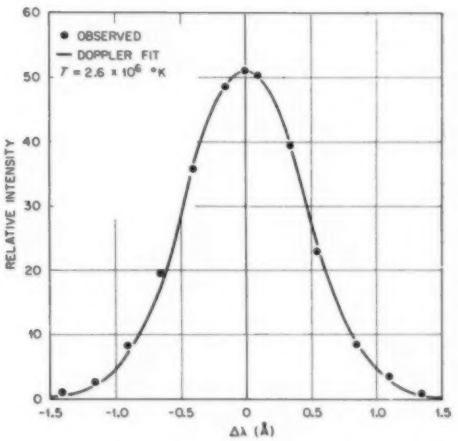

Fig. 14. Observed and fitted Gaussian profile of λ 3479 Å N IV in gas-fed carbon arc. 244-cm carbon arc, 149 A, 128 V, 8300 G, gas feed to cathode. Tank pressure: 9×10^{-6} torr.

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The concluding session went "Out of This World" first, only as far as the planets, as described by C. A. Barth *Jet Propulsion Laboratory*. In a talk entitled "Ultraviolet Spectra of Planetary Atmospheres", Barth traced the development of studies of the upper terrestrial atmosphere via rockets, and emphasized the advantages of flyby observations of the planets (which thus far have not been made in the ultraviolet, presumably due to payload mass restrictions). Barth explained that an extraterrestrial observer, using the solar illumination, would only be able to detect oxygen in the terrestrial atmosphere; similarly, charged-particle bombardment would only reveal the presence of nitrogen. The implications of these facts for the further study of the planetary atmospheres were developed; if Venus has a very weak magnetic field, no charged particles will reach the night side. The final speaker, G. J. Stanley *California Institute of Technology*, discussed "Characteristics of Radio Emission from Extragalactic Nebular". Although the radio astronomer has, other than the continuous spectrum, only a single line (the 21-cm *H*-spin flip) at his disposal, the development of the interferometer has made possible the acquisition of information of excellent angular resolution, and nebular anatomy can now be studied in parallel with the results of optical astronomy. Most radio nebulae are elliptical, not spiral. The range of radio observation should soon provide a critical test of opposing theories of cosmology. (Five radio stars have been identified in recent months, and red shifts as large as $^1/_2$ c have been observed. Some planetary information on Jupiter and Venus was also reported.)

The banquet speaker, D. S. Webber *Lockheed-California*, illustrated his talk on "Solar Flares" with moving pictures; one suspected from the tone and spirit of Webber's remarks that the late Robert Benchley deserved mention as a collaborator.

Attendance at the meeting was 132; and since the Bing Crosby Tournament was held a week prior to the WSA meeting, the celebrated golf courses of the Monterey Peninsula were relatively uncrowded—that is, by people other than spectroscopists. Information on the Western Spectroscopy Association can be obtained from the Recorder and Registrar, J. M. Gordon, Shell Development Company, Emeryville, California.

14th Annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pennsylvania, 4–8 March 1963

Reported by Stephen E. Wiberly, Rensselaer Polytechnic Institute

The 1963 Pittsburgh Conference lived up to the fine reputation established by its predecessors. Approximately 4000 scientists, including several hundred foreign visitors, participated. One of the outstanding features of this meeting was the convenience of having all the technical sessions and the equipment exhibits under one roof. Approximately 230 technical papers were presented over the five-day period, including 23 by scientists from Canada, England, Germany, Japan, Switzerland, and Uruguay. Three concurrent technical sessions were scheduled each morning and afternoon during the five days of the conference, and much of the research described involved such spectroscopic methods as emission, infrared, ultraviolet, mass, x-ray, and nuclear magnetic resonance.

The symposium on NMR spectroscopy of nuclei other than hydrogen was one of the highlights of the Monday sessions. A paper by Lauterbur dealing with NMR spectra obtained from one or more isotopes of about 60 elements indicated an important future role for NMR spectroscopy in inorganic chemistry. Studies on C^{13} were also reported, and Diehl *Switzerland* discussed measurements of O^{17} at natural abundance (0.04%), with the time of measurement involved being a few hours. One was reminded of the early days of infrared spectroscopy, when measurement of a single spectrum required several hours. On Tuesday afternoon, an interesting session was held on the storage and retrieval of analytical data. Of some bearing on this problem was a paper presented Wednesday by Savitsky at the Coblentz Society's symposium on techniques related to infrared spectroscopy. He discussed the application of computers in spectroscopy and, in particular, their use in extending instrumental performance by numerical filtering to reduce noise fluctuations and to improve effective spectral resolution. Of major importance is the data link between spectrophotometers and computers. Digital voltmeters or shaft-position encoders may be mounted on most conventional millivolt recorders to allow digital recording of NMR curves, chromatograms, spectra, or similar data. Can we look forward to the day when a sample is placed in a "universal spectrometer" and the absorption or emission spectrum from the x-ray to the microwave region appears digitized on tape? At the same Coblentz session, Lippincott described a technique for obtaining infrared spectra on microgram quantities using a cell with diamond or sapphire windows.

The papers in gas chromatography were devoted to new modifications of existing instruments and to a variety of analytical applications. Fluorocarbons were shown to be suitable absorbents and to have a distinct advantage for highly polar compounds that tend to give asymmetrical peaks in conventional columns. A paper co-authored by Rogers of Purdue reported some difficult separations at low temperatures using columns packed with such materials as $CuSO_4 \cdot H_2O$, $CdSO_4$, $MgCl_2 \cdot 2\ H_2O$, and Cu(pyridine)$_2NO_3$. Analysis of the pyrolyzed products of polymers by gas chromatography was one of the more novel methods presented. In the field of emission spectroscopy, the advantage of inert atmosphere excitation for the determination of trace elements in solution was again emphasized. Feldman reported on the improvements obtained with his porous-cup technique. He recommended carbon electrodes rather than graphite and use of waxed sidewalls and a helium atmosphere for excitation.

Some of the features of the instrument exhibit included several new infrared spectrometers, including one that scans continuously from 10,000 to 400 cm^{-1}. Gratings are replacing prisms even in the economy models. Other new developments included a wide-line NMR process analyzer for the determination of hydrogen, fluorine, and water; a new x-ray spectrometer; and an x-ray microprobe. This microprobe uses two magnetic lenses to produce an electron focus of 1–2 μ size and can make direct chemical analysis of a sample approximately 1 μ in area and 1 μ in depth, representing 1 pg of a material.

Meeting Reports *continued on page 726*

Use of Electrodeless Discharge Lamps in the Analysis of Atomic Spectra

Earl F. Worden, Ralph G. Gutmacher, and John G. Conway

The application of electrodeless discharge lamps in obtaining the information necessary for the analysis of the first and second spectra of lanthanide and actinide elements is discussed. It is shown how differentiation of neutral atom and first ion lines, self-reversal, and Zeeman-effect observations may be procured using these lamps as the sole source. The procedures are illustrated by studies on Cm, Gd, and Dy.

Introduction

The great need for increased spectroscopic investigation of the lanthanide and actinide elements has been pointed out by Meggers[1] and Moore[2–4] in their periodic status reports. These elements exhibit exceedingly complex spectra. In addition, many of them (particularly the heavier actinides) are either available in limited amounts or highly radioactive or both. For these reasons, an intense source, which emits sharp lines is highly efficient, and in which these elements are completely contained at all times is preferred. The electrodeless discharge lamp, which meets all of these requirements, has become the source of choice for the study of lanthanide and actinide atomic spectra.[5] The other advantages of these lamps have been comprehensively summarized by Meggers.[1]

The essential data needed for the analysis of a complex spectrum, besides an accurate, complete line list, are: (1) classification of the spectral lines as belonging to the neutral or ionized atom; (2) identification of resonance lines and other lines arising from transitions to low-lying levels of the atom, which may be derived from self-reversal; and (3) observations of Zeeman effect to obtain J and Landé g values of the energy levels. Many investigators of atomic spectra have used electrodeless discharge lamps in one or another of these phases of their work (see the compilation of references given by Moore[3,4]). We shall present a set of experiments showing how one may obtain all of the preceding information for the first and second spectra of a lanthanide or actinide element, using the electrodeless discharge lamp as the only source. Our experiments were chiefly conducted with elements $_{96}$Cm and $_{64}$Gd (as a prototype for Cm).

We shall briefly discuss the preparation of electrodeless lamps containing microgram quantities of a lanthanide or actinide in the form of a volatile halide. We shall then describe the methods of operating a lamp in order to obtain differentiation of ion and neutral atom lines, self-reversal, and Zeeman-effect observations, and the results encountered in each case.

Preparation of Electrodeless Discharge Lamps

High-frequency electrodeless discharge lamps containing elements with fairly high vapor pressures were described by Meggers and Westfall,[6] Jacobsen and Harrison,[7] and Zelikoff *et al.*[8] Corliss *et al.*[9] first constructed lamps containing metal halides. In 1957, Tomkins and Fred[5] described a method for the preparation of lamps containing about 1 mg of lanthanide or actinide as a pure halide. Bovey and Wise[10] have suggested some changes in their technique. They, like Tomkins and Fred, found that the iodide was preferable to chloride or bromide, since it gave longer-lived lamps.

In the method of Tomkins and Fred,[5] the lanthanide or actinide iodide is prepared by heating the oxide with anhydrous aluminum iodide at 500°C for 8 hr in a sealed tube. The product is then sublimed *in vacuo* into a carefully outgassed quartz lamp blank. Neon gas is added to a pressure of 2 to 3 mm Hg and the lamp is sealed off.

In the preparation of our lamps we essentially followed the method of Tomkins and Fred. With Cm, however, we desired to work with smaller amounts

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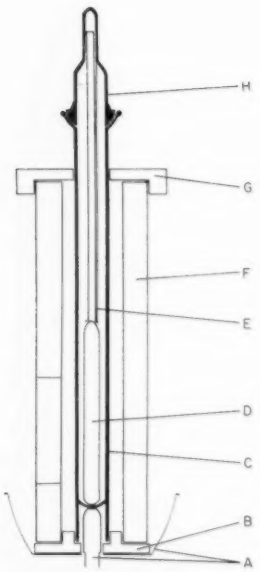

Fig. 1. Parabolic "A" director-furnace assembly: (A) microwave director, (B) transite insulator, (C) quartz chamber, (D) discharge lamp, (E) platinum wire (for initiating the discharge), (F) Cenco type 123-2 furnace element, (G) transite cap, (H) quartz chamber cap.

of material, starting with 100 μg of Cm_2O_3, since only limited quantities were available. The isotopic composition of the curium was 93% Cm^{244}, 3% Cm^{246}, and lesser amounts of other isotopes. It was desirable, in view of the high-alpha activity, to conduct the entire preparation in a glove-box enclosure, and slight modifications were made to the procedure to permit this.[11]

The first lamps we constructed were 100-mm long and had 7-mm i.d. These were found satisfactory for wavelength observations and for separation of the first and second spectra. For Zeeman-effect studies, smaller lamps 15 to 20 mm long with 3-mm i.d. were constructed, to permit operation parallel to the field[12] of a magnet with 2.54 cm gap. Following the work of Davison *et al.*[13] with Th, these lamps were made without carrier gas. The short lamps were found to show higher brightness, to work more efficiently with small amounts of material and to have an increased lifetime, perhaps due to less clean-up.

General Modes of Operation

The Raytheon Microtherm, which has a maximum output of 125 W at 2450 Mc/sec (12-cm wavelength), was used as the source of microwave radiation. To direct this radiation into the lamp, previous investigators have used either one of the directors for diathermy provided with the unit plus auxiliary heating equipment[5] or a microwave cavity.[8,10] We have used the parabolic "A" director-furnace assembly of Tomkins and Fred[5] for both long and short lamps, and also a 2.54-cm diam tuneable microwave cavity (designed by Fred[14] according to the general design specifications of Zelikoff *et al.*[8]) for operation in a magnetic field. These two assemblies are shown in Figs. 1 and 2. In all of our observations, the lamps were viewed from the side.

In beginning the operation of a lamp, it is placed in the field of the director or cavity and started with a discharge from a Tesla coil. Freshly prepared lamps containing no carrier gas will require initial heating (with a furnace or torch) to produce enough vapor pressure to start them. After some time of operation, enough free iodine will have accumulated to permit ready starting subsequently.

Details of operation of the lamps using a parabolic director-furnace assembly are given by Tomkins and Fred.[5] When a microwave cavity is employed, air cooling is essential to prevent burning a hole in the lamp and formation of cristobalite (crystalline quartz). Cristobalite formation will, in time, cause fracture of the lamp, and can occur if the lamp has been sealed off leaving a sharp point on the inside wall instead of a rounded surface. The brightness of a lamp operated in the microwave cavity is controlled by the flow of cooling air and the position of the tuning stub, and, of course, by the input microwave radiation obtained from the Microtherm.

The temperature of operation controls the metal vapor pressure inside the lamp. At low pressures the

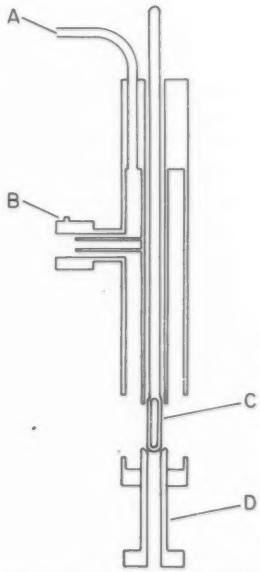

Fig. 2. Microwave cavity; (A) cooling air inlet, (B) input connector, (C) discharge lamp, (D) threaded tuning stub. The diameter of the cavity is about 2.5 cm.

complete diameter of the lamp emits light. At high pressures the discharge is confined to a bright center column.

Differentiation of First and Second Spectra

The general practice for sorting atomic and ionic lines in the past has been to compare their intensities in two different sources. Commonly, these sources have been conventional dc arcs and high-voltage ac sparks, but hollow cathodes and high-temperature furnaces have also been used to supplement or substitute for dc arc studies. The relatively low first-ionization potentials characteristic of the lanthanides make separation of their first and second spectra difficult. Fassel *et al.*[15] have suggested that flame spectra may provide for the lanthanides a simple means of identifying lines originating from low-lying states in the neutral atom. Mitchell[16] has described operating conditions by which a hollow cathode may be made to emit predominantly either neutral atom or first ion lines. We have produced a similar effect by varying the operating conditions of electrodeless discharge lamps, and have used it to classify first and second spectra.

Electrodeless discharge lamps emit predominantly first-spectrum lines and the strongest lines of the second spectrum. Several authors[5,17] have shown that the relative intensities of lines of the first and second spectra vary with the vapor pressure of the element in the lamp. At low-vapor pressure lines of the second spectrum are relatively favored, whereas at high-vapor pressure, the first spectrum is enhanced.

By varying the operating conditions, using either the director-furnace assembly or the cavity, the vapor pressure of the metal in the lamp can be altered. No definite set of instructions can be given which will apply to every lamp, since each metal halide and each lamp will of course behave differently. As guideposts, we cite the following from our experience with Cm and Gd.

In these experiments, we used the parabolic "A" director-furnace assembly with either the long or short lamps. A series of exposures (usually 3 to 5) was taken, operating the lamp at a different, higher furnace temperature (i.e., higher metal vapor pressure) for each exposure. The light output from the lamp should be kept constant during any one exposure. It was found best to precondition a lamp by heating it in operation to the highest temperature to be used, holding it there for 5 to 10 min, and then allowing it to cool well below the lowest furnace temperature to be used, before starting the series of exposures. For long lamps containing about 100 μg of the triiodide of Cm or Gd, the furnace temperatures ranged from 500° to 750°C; short lamps were operated at 400° to 600°C. The spectra were photographed with a 3.4-m Ebert spectrograph in the second order of a 1200 line/mm grating, giving a reciprocal linear dispersion of 1.2 Å/mm. In photographing the spectra, as the lamp becomes brighter at higher metal vapor pressures, one reduces the exposure time proportionately, to keep the increase in total integrated light reaching the plate to 20–30%. We were able to

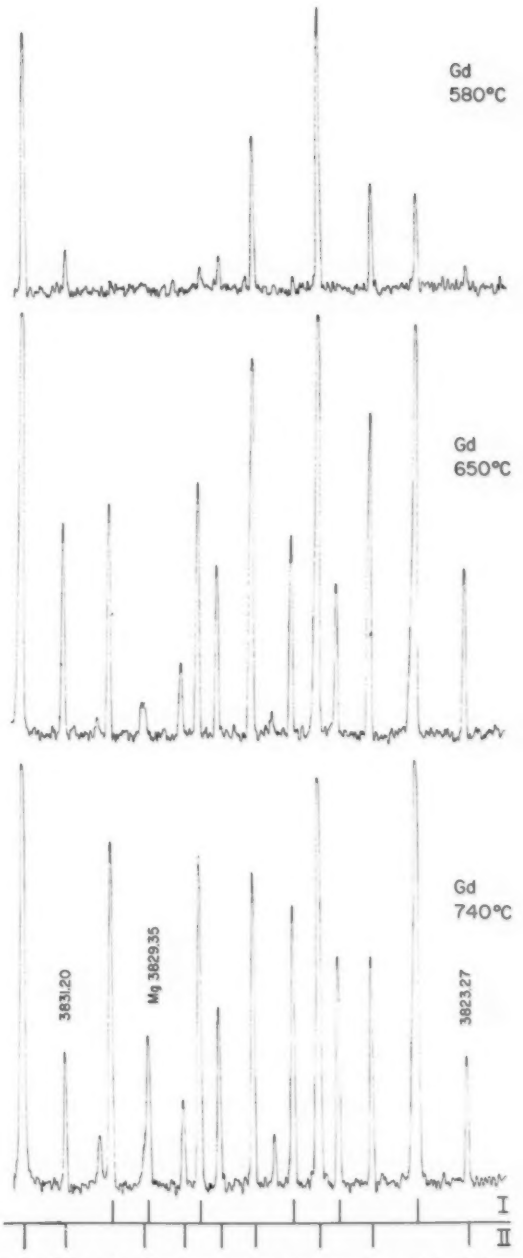

Fig. 3. Microdensitometer traces of a portion of the Gd spectrum, showing the effect of increasing metal vapor pressure on the relative intensities of neutral atom and first ion lines. Exposure times are: 10 min, 580°C; 8 min, 650°C, 7 min, 740°C. A long lamp was used. First and second spectrum lines are indicated according to the assignments of Russell[18] and King.[19]

estimate the proper exposure times visually, after some experience. Two valuable aids in conducting these experiments are a furnace temperature controller and some type of light meter* to aid in judging exposure times. These items have been recently added to our equipment.

The microwave cavity can be used in a manner similar to the director-furnace assembly. Line-voltage regulation is quite important here.

In a correctly taken series of exposures, the first-spectrum lines become progressively stronger by a factor of 2 to 4 for weak, medium, and moderately strong lines. Second spectrum lines decrease in relative intensity by the same factor or change little in intensity. Assignments can thus be made visually directly from the plate. Very strong lines, which are approaching saturation, will show much less change (in unfavorable cases, only 10–20%), but the eye can still clearly distinguish whether the intensity is increasing or decreasing. A microdensitometer can be used to help resolve doubtful cases. Figure 3 shows microdensitometer traces of sections of Gd spectra obtained at three different temperatures. The spectrum assignments shown are due to Russell,[18] who derived them from the temperature classifications of King.[19]

From our plates we have sorted some 400 lines of Gd of all intensities between 2900 and 5000 Å as neutral atom or first ion lines. A detailed comparison showed 96% agreement with Russell's assignments and King's classifications. Seventy lines were assigned independently by two of the authors; there was disagreement in only two cases.

These results gave us the confidence to proceed with Cm. The effect of varying the metal vapor pressure in lamps containing the iodide of this element is shown in Fig. 4. At the time of writing, the spectral range from 2700 to 4900 Å has been examined and approximately 5000 lines have been assigned to the first or second spectrum. This information is to be extended to cover the range from 2400 to 9000 Å and will be published at a later date.

A word of caution is in order. Self-absorption of the lines can lead to misinterpretations unless it is recognized. Neutral atom lines will behave like first ion lines if self-absorption is present, since with increasing vapor pressure of the metal the intensity of the line will be decreased by increasing self-absorption. This effect occurs mainly with strong lines. At sufficiently high vapor pressures, these lines will show self-reversal, provided a spectrograph with high dispersion is used. We shall discuss this in detail in the section dealing with self-reversal. Should the presence of self-absorption be missed, correct results can still be obtained, since for the final assignment of spectrum to each line, intensity ratios, self-reversal, and Zeeman data should all be taken into consideration.

Self-Reversal

Information on lines arising from transitions to the ground state or to low-lying levels of the atom is most useful in the analysis of the spectra of lanthanides and actinides, and of elements generally. Such lines may be recognized by the fact that they are self-reversed when excited by suitable sources. Sugar[9] has reviewed the light sources used for observing reversed lines and has described a high-current arc which may be used to produce self-reversed lines in the spectra of the lanthanides.

It is known that self-absorption and self-reversal occur in the spectra emitted by electrodeless discharge

Fig. 4. Differentiation of the first and second spectrum lines of Cm. Exposure times are: 4 min, 530°C; 2 min, 600°C. A short lamp was used. The spectrum assignments are by the authors.

* Our light meter consists of photomultiplier tubes placed inside the spectrograph, with necessary optics to intercept a small portion of the undispersed light before it reaches the collimating mirror and direct it to the photomultiplier tubes (R. G. Gutmacher, unpublished work).

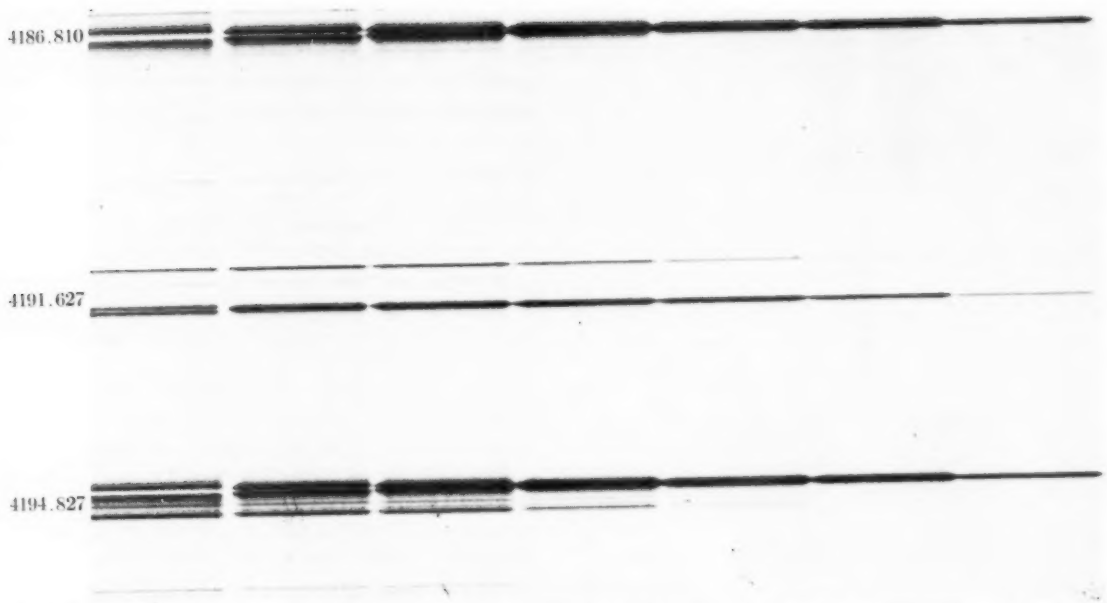

Fig. 5. Self-reversal of Dy first-spectrum lines produced at increasing metal vapor pressures. The source was a short DyI_3 lamp operated in the microwave cavity. The exposures were taken with the Argonne National Laboratory 9.15-m spectrograph in the second order of a 600 line/mm grating (plate factor 0.78 Å/mm). Wavelengths of the reversed lines are given.

lamps[5,9] and most workers have operated them in such a manner as to avoid this effect. We, on the contrary, have obtained much valuable information by operating the lamps at high temperature in order to produce self-reversed lines. Long lamps with only 100 μg of material could not be used for this purpose,* but when the short lamps were operated at high temperature, self-reversal was quite apparent. The effect is shown for Dy in Fig. 5. The short lamps were either run in the cavity, or placed in the field of the parabolic director and heated with a flame. (The furnace assembly was not used for this application, since it absorbs some of the microwave energy and poor coupling results, so that at high-metal vapor pressures the lamp may be extinguished.) The lamps should be operated at maximum brightness. To observe reversal, a spectrograph giving a minimum dispersion of 1 Å/mm is required. We have made most of our observations with a 3.4 m Jarrell–Ash Ebert spectrograph in the 10th through 14th orders of a 300 line/mm grating, using the Order Sorter. Plate factors were 0.8 to 0.6 Å/mm. Even higher dispersion is desirable.

Self-reversal was first studied with short lamps containing GdI_3. Approximately 200 reversed lines were found. Comparison with Russell's[18] assignments showed that all of these lines involved combinations with low-lying levels (0 to 18,000 cm^{-1}); the majority involved combinations with the ground term levels (0 to 1719 cm^{-1}). This shows that one obtains about the same information by this technique as by using a King furnace or by using the source described by Sugar,[20] neither of which is applicable for limited samples of radioactive elements.

The self-reversal studies were next extended to Cm. Again approximately 200 reversed lines were found in the range from 3000 to 5100 Å. With these lines we were able to derive a ground term level scheme for Cm, using a constant differencing program. This scheme was confirmed by additional lines taken from our listing of first spectrum lines and by Zeeman data.[21] The technique described here has since been applied successfully by others in extending the analysis of the spectra of Pu,[22] Pa,[23] and Np.[24] In addition, reversal has been observed with discharge lamps containing the iodides of Ce, Pm, Sm, Eu, Tb, Dy, Ho, and Er.

In the operation of electrodeless discharge lamps at high metal vapor pressures, a bright central column is formed. This is surrounded by cooler layers which predominantly contain thermally excited neutral atoms. The sheath also contains a smaller number of ions. Thus, some second-spectrum lines will also show self-reversal, but much less so than first-spectrum lines. The two can generally be distinguished from each other by their appearance. Reversed first-spectrum lines generally show wide wings, while second-spectrum lines are sharp with a narrow reversed section. A few reversed second-spectrum lines have been observed in the

* Self-reversal has been obtained with long lamps containing 1 mg or more of material.

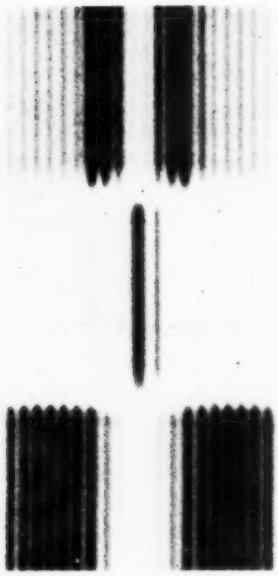

Fig. 6. Self-reversal and Zeeman pattern of Cm II 3498.778 Å, $J' = J'' = 7/2$. Photographed in the 7th order of the ANL 9.15-m spectrograph. The Cm^{246} isotope shift line appears to the right.

spectra of Dy and Cm and confirmed by Zeeman patterns. Figure 6 shows an example of such a line in the Cm spectrum.

Zeeman Effect

Electrodeless discharge lamps have been used very successfully by several workers to obtain Zeeman-effect observations.[17,22,25–28] They have employed magnetic fields varying in strength from 24,000 to 80,000 G. In conventional sources, the second spectrum is favored in a magnetic field. If electrodeless lamps are used, the intensities of the first and second spectra are approximately equal[25] (cf. Fig. 7).

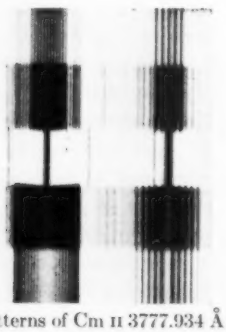

Fig. 7. Zeeman patterns of Cm II 3777.934 Å and Cm I 3779.963 Å, showing that first-spectrum lines appear with good intensity in the spectrum emitted by a lamp operated in the magnetic field of 24,000 G. Photographed in the 6th order of the ANL 9.15-m spectrograph. The two lines have approximately equal intensities when emitted by a lamp operated at medium pressure.

If there is weak coupling of the microwaves to the lamp, it is usually necessary to operate the lamp parallel to the magnetic field.[12] In one set of experiments with lamps containing Gd or Cm iodide, we employed a parabolic "A" director cut down on the sides so that the center probe could reach the center of the magnetic field. The field strength was 28,750 G, and the width of the gap and the diameter of the pole faces were each 2.54 cm. In these experiments, the microwave coupling was not very efficient and the lamp would not operate perpendicular to the magnetic field. It was also necessary to supply additional heat to the lamp by means of several turns of #22 nichrome wire connected to two 6-V storage batteries. (The ripple of rectified power supplies is often sufficient to shake the coil.) A resistor was in series with the windings to control the temperature of the coil. The coil produces an added magnetic field, which is not reproducible. It is, therefore, necessary, when using this arrangement, to calibrate the field by means of the Zeeman patterns of impurities contained in the lamp.

Fig. 8. Zeeman pattern of Cm I 3522.355 Å showing reversed components. Photographed in the 6th order of the ANL 9.15-m spectrograph. The predominant isotope (93%) is Cm^{244}. The isotope shift line of Cm^{246}, which appears at 3522.409 Å, complicates the spectrum.

It is more convenient to make Zeeman-effect observations by operating the lamp in the cavity. In this method of operation we employed a magnet with a field strength of 24,000 G and photographed the Zeeman patterns with the 9.15-m spectrograph of Argonne National Laboratory. Representative patterns of first- and second-spectrum lines obtained by us are shown in Fig. 7.

When a cavity is used, the lamp is of course placed perpendicular to the magnetic field. The coupling of microwaves to the lamp is then so efficient that it is necessary to cool the lamp by blowing air through the cavity. Operating a lamp at very high intensity in a magnetic field greatly shortens the useful life of the lamp. High temperature operation of the lamp yields Zeeman patterns with broadened or self-reversed components. A pattern with self-reversed components is pictured in Fig. 8. We have observed all variations

from complete reversal of all the components to reversal of only the strongest components, the others being normal. Where the line is completely absorbed in the center and only the wings are left, difficulties may arise in the interpretation of the Zeeman patterns. One could interpret the wings as individual lines and thus count more components than are there and miscalculate the J value. To avoid such errors, it is advisable to take a series of exposures at low and medium intensity of the lamp.

Conclusions

The use of electrodeless discharge lamps as light sources in the study of atomic spectra of lanthanides and actinides has been described, and illustrated with elements $_{96}$Cm and $_{64}$Gd. It has been shown how differentiation of the first and second spectra, self-reversal, and Zeeman-effect observations may be obtained. These methods have been used successfully on a number of lanthanide and actinide elements by ourselves and by other investigators. Although we have confined our discussion to the study of lanthanide and actinide spectra, for which electrodeless discharge lamps are especially advantageous, these procedures should be generally applicable to other elements as well.

We are very grateful to Mark Fred for the use of the equipment at Argonne National Laboratory and for much valuable aid and consultation. We are indebted to E. Kenneth Hulet of this laboratory for purification of the Cm and for advice and assistance in handling radioactive material. We wish to thank Frank S. Tomkins and Sumner P. Davis for many helpful discussions.

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SOME OSA DIRECTORS

David Richardson *Bausch & Lomb* (left), W. Lewis Hyde *Rochester*, and John N. Howard *AFCRL*.

Mary Warga *OSA* and Georg Hass *ERDL*.

photos D. L. MacAdam (*See also page 733*)

From the Editor

In this issue on Spectroscopy one may be taken somewhat aback by the happy abandon with which authors wander from angstroms to millimicrons to nanometers. This is an area of terminology where opinion is not yet firm. We discussed this matter recently with one of the editors of *Spectrochimica Acta*. He also permits all of these units, although he reminds those authors using whole-number millimicrons that they are implying an accuracy of only ± 5 angstroms in their spectral measurements. We were also happy to note that he dislikes micrometer, μm, instead of micron, μ, just as much as we do. Matters such as this will no doubt provide yet many a scholastic disputation.

Although in general we try to adhere to the AIP *Style Manual* for this journal we have recently decided to prefer *wavenumber* as one word, rather than the two-word noun and hyphenated adjective (e.g., *wave-number* interval) of the *Style Manual*. This conforms more to the accepted practice of most spectroscopists, to such journals as *J. Mol. Spectry.* and *Spectrochim. Acta*, such books as Harrison, Lord, and Loofbourow, and seems to us to be more analogous to the usage of wavelength as one word.

Strictly speaking, wavenumber represents a concept rather than a unit; and just as a wavelength may be in units of microns, millimicrons, or angstroms, so also a wavenumber may be in units of waves per centimeter (reciprocal centimeters, cm^{-1}) or in reciprocal meters. In spite of this, in the minds of most molecular spectroscopists it is understood that wavenumbers are in cm^{-1} just as implicitly as the knowledge that frequency always means cycles per *second* rather than, say, cycles per minute or per hour. One paper soon to appear has used the term kayser to mean the unit cm^{-1}. This unit has not appeared in this journal since p. 5 of the first issue. This unit has its staunch advocates but perhaps even stauncher opponents, and it is not considered an approved unit by AIP. The use of kayser for cm^{-1} is somewhat like the use of torr for mm Hg. Some opponents simply say, "why name it?" Called by whatever name it is still a reciprocal centimeter and does not have the ancient historical claims of similar artificially named units such as the angstrom. Other opponents claim it would cause confusion in molecular spectroscopy as it frequently occurs in $h\nu/kT$. If the Boltzmann constant is a lower case k and the temperature is °K, do we want the units of ν to be yet another K?

While we are discussing matters of spectroscopic nomenclature let us consider how one defines the limits of the wavelength regions of the ultraviolet or infrared. It is true that words like "near" and "far" can mean very different things to different people. When photographers refer to the infrared they ordinarily mean the region accessible to infrared-sensitive film which extends only to slightly beyond 1 μ. Similarly, the "infrared" photomultipliers with the S1 sensitive surface extend only to perhaps 1.1 μ, which is about where most infrared workers consider the infrared to begin. Some Europeans have the interesting definition of "far-infrared" as that portion of the infrared spectrum where the infrared source is the self-emission or thermal radiation of ordinary materials, whereas the "near-infrared" is that region where one measures only reflected sunlight from substances. Thus they would say that the early Tiros satellites with infrared photomultipliers or PbS sensors, which could function only over the sunlit side of the earth, were working in the near-infrared, but one with a sensor for the 8–13 μ region, sensing the thermal radiation of the earth itself (or its atmosphere) was operating in the "far infrared".

To most infrared people, however, the "far infrared" means that region beyond the spectroscopic grasp of usual prism materials. In the rocksalt days this was beyond about 15 μ; with the availability of CsI prisms the boundary has moved out to about 50 μ. In a report on the Transactions of the Triple Commission for Spectroscopy which appeared in *J. Opt. Soc. Am.* **52,** 476 (1962) the following nomenclature was recommended:

The "near infrared" means the region from 0.8 to 2.5 μ or 12,500 to 4000 cm^{-1}.

The "mid infrared" means the region from 2.5 to 50 μ or 4000 to 200 cm^{-1}.

The "far infrared" means the region from 50 to 1000 μ or 200 to 10 cm^{-1}.

We have been gently encouraging our authors to conform to these recommendations.

At the other end of the spectrum similar controversy rages concerning which is ultraviolet, middle ultraviolet, far ultraviolet, and extreme ultraviolet. Here there seems to be some uniformity in calling 2000–3000 Å the middle ultraviolet, 1000–2000 Å the far ultraviolet, and shorter than 1000 Å the extreme ultraviolet.

We prefer the abbreviation xuv advocated by Tousey [*J. Opt. Soc. Am.* **52,** 1186 (1962)] to euv, although both forms have previously appeared in the journal. Tousey's argument was that x not only suggests "extreme" better than E but also neatly closes the span between uv and x rays.

Jean Lecomte once suggested that the spectrum be classified in approximate "octaves" up or down from the visible, the central "octave," 4000 to 7500 Å. (So also does Dr. Humphreys elsewhere in this issue.) Thus we would have regions 1000–2000 Å, 2000–4000 Å, 4000–7500 Å, 0.75–1.5 μ (photographic ir), 1.5–3 μ (PbS ir), 3–6 μ (InSb ir), 6–12 μ (rocksalt ir), 12–24 μ (KBr ir), 25–50 μ (CSI ir), 50–100 μ (reststrahlen ir), and so on into the far far ir.

Another characteristic of spectroscopists is that each tries to define his region in such a way as to include all the others as subsidiaries. Thus, the ir man will reason that since he already embraces 0.7 to beyond 1000 μ one might as well throw in the residual 0.7 μ interval (the "hard ir") for good measure. Dr. Weissler says he finds it easier to think in terms of the energy of the photons: at 100 Å this is 124 eV, at 1000 Å it is 12.4 eV; by the time one reaches 1 μ the energy is only 1.24 eV and surely beyond that it is completely negligible. All of these spectroscopists dismiss the entire microwave region with the same argument: there is more energy between the two Na D lines (18 cm^{-1}) than in the entire microwave region, with the mm and half of the submillimeter region thrown in.

Both the uv and the ir people will agree heartily, however, that the visible region is passé, a no-man's land, a worked out gold mine. What thrill, what mystery is there in something you can see? (Let us hasten to add that we do not share this opinion; this issue demonstrates the current vitality of the visible region.) One should note that even this region has poorly defined limits; most of us do not see much below 4000 Å or beyond 7000 Å, although there are cases on record for example of people who have seen the rubidium line at 7800 Å.

Although optics had its humble beginnings in the visible it has long since spilled over its banks and engulfed most of the electromagnetic spectrum. One now sees symposia entitled "Optics and Spectroscopy of All Wavelengths." At a recent IRE meeting on millimeter and submillimeter waves a good part of the speakers and of the audience were people we ordinarily consider optics people. Instead of feeling aggrieved that these other groups are attempting to usurp optics we should rather rejoice that the field is being appreciated by people trained in other disciplines. It is our hope that this journal can become the publication medium for these other workers now turning to optics.

JOHN N. HOWARD

Wavelength Measurements with a Concave Grating Spectrograph

Frank S. Tomkins and Mark Fred

Certain disadvantages and limitations in conventional methods of measuring wavelengths from grating spectrograms are discussed, and some alternative procedures described. It is shown that by fitting thorium standards to the dispersion of the Argonne 9.15-m spectrograph, using a polynomial least-squares program with a digital computer, wavelengths accurate to 1 in 10^8 can be obtained at a rate of 1000 per day.

I. Introduction

The concave grating spectrograph has been used extensively for the routine measurement of wavelengths of spectrum lines for some eighty years. All of these measurements have been empirical in that the positions of the lines on the photographic plate were compared with the positions of standard lines which had previously been measured interferometrically. Interferometric methods are more accurate and have the fundamental advantage that all lines can be measured against a single standard. Grating measurements, however, are much faster, and for term analysis, which has usually been the ultimate purpose, their accuracy has in the past been sufficient. In recent years, with emphasis on very complex spectra, this is no longer the case when the conventional procedure is used. Moreover, there is the practical difficulty that each complex spectrum requires the measurement of many thousands of wavelengths and the conventional procedure is too slow. The result of these two factors has been a severe reduction in the number of term analyses reported, in spite of the availability of many new rare-earth and heavy elements. It must be emphasized, however, that the difficulty with grating wavelengths has not been an inherent one, but due largely to the poor quality of the standard lines available and to the computational procedure. This paper describes our attempts to overcome these limitations.

II. Properties of the Concave Grating

The theory of the concave grating has been developed by a number of authors starting with Rowland and culminating in the treatment of Namioka.[1] For our purposes the higher order aberrations are not significant and only the fundamental equation needs to be considered:

$$p\lambda = d(\sin\alpha + \sin\beta). \tag{1}$$

Here p is the order, λ the wavelength (in laboratory air), d the grating space, α the angle of incidence, and β the angle of diffraction. We shall be concerned primarily with the Paschen-Runge mounting, illustrated in Fig. 1. Here R is the radius of curvature of the grating, equal to the diameter of the Rowland circle on which the slit and photographic plates are mounted. The angle β is equal to x/R, where x is the distance from the grating normal to the spectrum line, measured along the circle:

$$p\lambda = d\sin\alpha + d\sin(x/R). \tag{2}$$

The reciprocal dispersion or plate factor is

$$\frac{d(p\lambda)}{dx} = \frac{d}{R}\cos\beta. \tag{3}$$

Over the region which can be measured on one plate (usually 25 cm) the change in dispersion is not great but cannot be ignored.* For example, for a 9.15 m, 600 lines/mm grating and $\beta = 0.2$, the wavelength at the middle of a 25-cm region differs by 0.334 Å from that computed assuming linear dispersion over the region. In the past it has been customary to take account of the change in dispersion by a graphical method in which a correction curve is plotted giving the errors obtained for known standard lines assuming linear dispersion. The usual standards have been iron lines obtained in a dc arc operated according to I.A.U. specifications.[2] The difficulty has been that the iron arc lines are too poor in quality and specified wave-

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* Except near the normal. This is, of course, the reason for Rowland mounting.

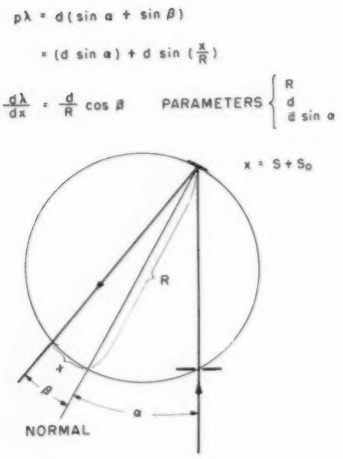

Fig. 1. The Paschen-Runge grating mounting.

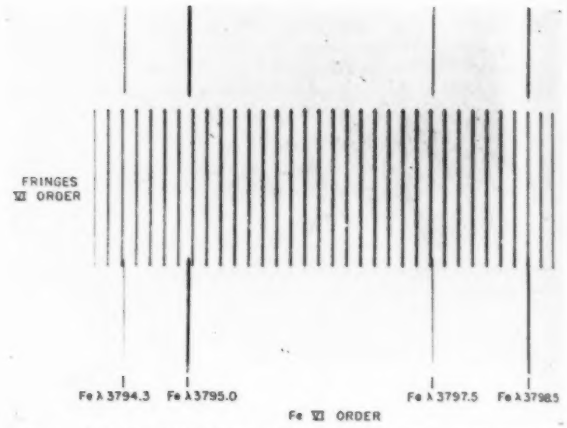

Fig. 2. White light fringes taken with a 5-mm interferometer spacer, corresponding to 1 cm^{-1} between fringes. The Fe lines were produced in a hollow cathode.

lengths, and are also too few for large spectrographs. The result has been that the points scatter about a smooth curve and leave large gaps, leading to an uncertainty in the correction curve which is considerably larger than the measuring error.

The difficulty with the standards has been recognized for some time,[3] but when the present program was initiated, it appeared that better standards would not be available for a long time to come, so other methods were considered. Some of these are now obsolete but are still of interest.

III. White Light Fringes as Wavelength Standards

One possible solution to the standards problem appeared to be the use of Edser-Butler fringes previously adapted to infrared measurements.[4] These fringes are produced by passing light from a source having a continuous spectrum through a Fabry-Perot interferometer and focusing the fringes formed at infinity on the slit of the spectrograph. The fringe pattern on the slit consists of the usual sets of Fabry-Perot rings, one set for each wavelength in the source. There will be a bright spot at the center for wavelengths for which the interferometer spacer is an integral number of half-wavelengths. By using a short slit opening these wavelengths can be admitted to the spectrograph and other wavelengths rejected. Because of the astigmatism of the spectrograph these wavelengths appear as spectrum lines, equally spaced on a wavenumber scale (Fig. 2). The spacing in cm^{-1} between fringes is given by the usual formula for the interferometer free-spectral range, $t/2$. The width of the fringes is determined by the resolving power of the interferometer, the resolving power of the spectrograph, and the height of the slit. In practice (Fig. 2) the width of the fringes is of the order of ten times the width of a spectrum line, but it is symmetrical, and so measurable with a photoelectric setting comparator without much loss of accuracy.

The spacer can be measured in the usual way by determining the order of interference of three standard lines from ring diameters using a stigmatic spectrograph. It was found to be more convenient, however, to use the Paschen-Runge spectrograph by interpolation between fringes of the positions of the standard lines photographed with the interferometer removed. This procedure is also somewhat more accurate because the interpolation is essentially linear. With a 0.5-cm spacer, corresponding to 1 cm^{-1} between fringes, the order can be determined to ± 0.001 for, say, λ 3700 Å measured in the VI order of the spectrograph.

The unknown wavelengths are measured in the same way, by determining by interpolation what the fractional order of interference would be if the interferometer were used in the conventional way. Usually, the line to be measured is known sufficiently well to specify the whole order of interference, or alternatively this can be established from the dispersion of the spectrograph alone. The wavelength in laboratory air is then twice the spacer thickness divided by the order of interference. As an example of the capabilities of the method some measurements of iron hollow cathode lines are listed in Table I. The table indicates an average error of something in the fourth decimal place. It also illustrates how a slight asymmetry in the line shapes can affect the measurements by introducing a dependence on intensity.

In the procedure outlined above it is necessary to measure only the fringes adjacent to the unknown line, although a small increase in accuracy results if several fringes on each side are measured and averaged. As originally conceived it was planned to use the fringes as a wavenumber scale to measure from a standard line, but this method involved counting large numbers of

Table I. Iron Hollow Cathode Wavelengths Measured by White Light Fringes

True λ[a]	Measured λ	(T − M) in 10^{-4} Å	Intensity[b]
3687.4560	0.4560	0	46,000
3709.2458	0.2456	2	57,300
3727.6187	0.6187	0	51,900
3734.8643	0.8631	12	473,000
3743.3614	0.3614	0	39,900
3749.4852	0.4843	9	326,000
3758.2326	0.2320	6	207,000
3763.7887	0.7885	2	115,000
3767.1912	0.1918	−6	71,600
3787.8800	0.8800	0	28,200
3795.0017	0.0025	−8	38,000
3798.5110	0.5115	−5	26,400
3799.5468	0.5473	−5	37,800
		Av ±4.2	

[a] Trans. Intern. Astron. Union **10**, 216 (1960).

[b] H. M. Crosswhite, Johns Hopkins Spectroscopic Report No. 13 (1958).

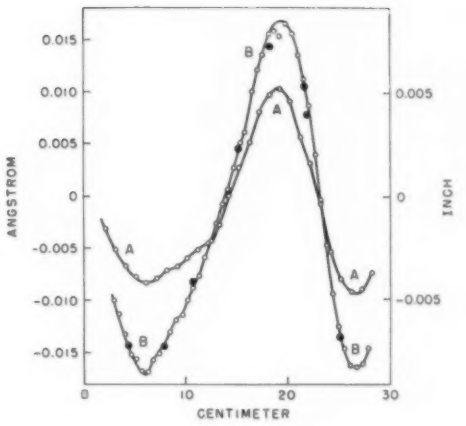

Fig. 3. A. Deviation in radius of the plateholder for the region of the circle used for Fig. 2. and Table I. B. Errors in wavelengths of white light fringes computed by the grating equation. The iron lines are indicated by the black dots.

fringes with risk of miscounting. A solution attempted to overcome this difficulty was the use of modulated fringes obtained from a compound interferometer,[5] but the interpolation procedure with prior knowledge of the whole order of interference was found more convenient.

The advantages of white light fringe standards are: (1) their wavelengths can be computed with high accuracy once the spacer length is determined (this advantage has since disappeared with the availability of thorium standards[6] discussed below), and (2) the standards are quite close together, so interpolation is independent of irregularities in dispersion due to plateholder irregularities, distortion from plate clips, nonuniform photographic emulsion shrinkage, etc. (This advantage remains.)

The disadvantages are: (1) the procedure is more time-consuming than direct comparison with thorium standards; (2) the necessity for a short slit for the fringes results in considerable light loss for the unknown spectrum (to change the slit height between exposures may lead to shifts due to line curvature); (3) a change in barometric pressure produces a change in the position of a spectrum line but not in the positions of the fringes (if the interferometer case is left open to the atmosphere, which is the most straightforward procedure to handle); hence, the correction of the observed wavelength to standard air is much more severe than from the differential shift of a standard comparison line; (4) suitable white light sources are not available for all spectral regions, and bandpass filters must be used to avoid overlapping in high orders of the spectrograph, whereas much more overlapping is acceptable for, say, thorium standards.

In summary one may say that white light fringe standards probably permit the highest accuracy in wavelength measurements with a concave grating spectrograph by reducing the requirement for a smooth dispersion, but the method is more difficult than is usually warranted.

IV. Absolute Wavelength Measurements by Means of the Grating Equation

A. Spectrograph

The Argonne 9.15-m Paschen-Runge spectrograph[7] was initially constructed to have a radius which was constant around the circle to well within the depth of focus (0.5 mm). When the difficulties with the graphical correction procedure for nonlinear dispersion using iron arc standards were appreciated, the fact that the circle was nearly uniform suggested the direct application of the grating Eq. (1). This approach has the further advantage that all computations can be done by means of a digital computer, including the conversion to vacuum wavenumbers using the Edlén dispersion formula,[8] with other advantages to be described later. We write

$$p\lambda = d\sin\alpha + d\sin\left(\frac{s + s_0}{R}\right), \qquad (4)$$

where s is the comparator reading in millimeters for the line being measured and s_0 is a constant derived from the reading for a standard line.* It soon became clear, however, that the remaining irregularities in the plateholder were much too large to ignore. This can be seen from Fig. 3, which shows the errors obtained for white light fringes for the region of the circle used for Table I. Most of the error is due to the plate clips spaced

* Wavelengths so determined are not quite absolute in that they are not completely measured by geometry, as they would be if measured from the grating normal, but much more absolute than empirical, and the description is adopted for convenience.

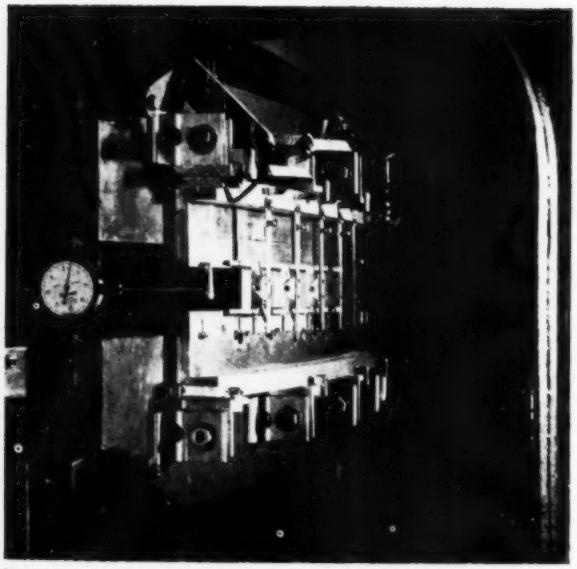

Fig. 4. Plateholder sections with dial indicator and 5 × 46 cm. plate.

every 11.4 cm, which distorted the plate and also compressed the continuous steel strip which constituted the focal surface.

It appeared that these difficulties could be overcome by substituting machined castings for the original adjustable circle, using a radius-generating fixture available in the Argonne shops.[9] The structure adopted after considerable experimentation is shown in Fig. 4. The upper and lower plate rails are made of special high stability magnesium-aluminum alloy castings of L-shaped cross section. Each section is 122 cm long, supported at five points by pairs of angle stock brackets so as to give all degrees of freedom. The sections were adjusted by means of the radius arm shown in Fig. 5, which has increased rigidity and more precise bearings than the original.[7] Each piece was mounted with the ends at the proper distance from the center of the circle as measured with a dial indicator. The center of the piece (once the radius generating fixture in the shop had been adjusted by trial and error) was then within 50 μ of the proper reading, and this error could be reduced to 2.5 μ by flexing the piece by finger pressure alone. Thus the radius of each piece was correct to 2.5 μ at three points 61 cm apart, under negligible strain, and, since the piece was originally machined with a continuous 122-cm stroke, the expectation was that between these three points the radius could not be far off. Adjustment of the fourth and fifth pairs of brackets 30.5 cm from each end was attempted so as to minimize the residual errors. Unfortunately, it was found that the curvature was comparatively irregular and could not be made uniform by any amount of forcing of the remaining brackets. The irregularities varied from piece to piece and were apparently due to warping after the original strains were relieved by the machining. When this was realized the pieces were remachined and were then found to be much more uniform, the maximum error in radius becoming 12.5 μ. It was evident that it would be very difficult to accomplish any substantial further reduction of the irregularities in curvature by machining the pieces in the shop. It appeared possible that the pieces mounted on the circle could be improved *in situ* by grinding or lapping with the aid of the radius arm. This was deferred, however, to gain experience within the present limitations, in view of the considerable effort which would be required and uncertainty about the long term stability. It has since been found more feasible to correct for the residual errors in the computation than to try to eliminate them (Sec. V).

It should, perhaps, be pointed out that high accuracy in the construction of the plateholder is necessary in order to use the grating equation because the positions of spectrum lines can be measured with high accuracy, i.e., to one wavelength of visible light. Reference to Fig. 6 shows that for $\beta = 45°$ (a commonly used region of the Argonne spectrograph) an error in radius of 12.5 μ produces a shift of about the same magnitude in the line position on the photographic plate. Thus if the standard line falls at A in Fig. 6 and the line to be measured at B the measured separation will be in error by an order of magnitude greater than the setting error. On the other hand, if the two lines fall at positions corresponding to B and C both will be displaced by about the same amount and the measured separation will be nearly right. This argument indicates that small errors in radius can be tolerated if the changes in curvature are gradual compared with the distances between unknown and standard lines, which average 10 cm or less. The present errors in the plateholder thus are considered acceptable. Another aspect which leads to relaxed tolerances is the fact that the wavelength measuring procedure requires greatly reduced effort, making

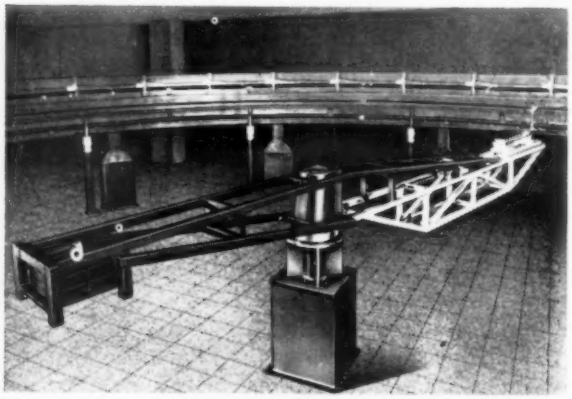

Fig. 5. Radius arm.

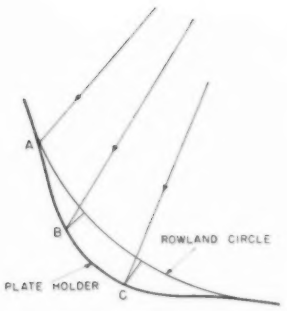

Fig. 6. Effect of plateholder deviations.

it feasible to measure the same line in a number of grating orders and average the results.

B. Comparator

Wavelength measurement by means of the grating equation requires, in addition to a precise plateholder, a convenient way of performing the computations. It is possible to solve Eq. (2) by means of a desk calculator and tables of the trigonometric functions, but the process is tedious and not to be considered because of the availability of digital computers. To reduce further the effort involved, the photoelectric setting comparator[10] has been modified to provide punched card output which serves directly as input to the computer.

The card output is obtained by means of an analog-to-digital encoder* coupled to the comparator screw. The encoder is a disk with concentric metallized sectors providing 2000 contacts per revolution, corresponding to a least count of 0.5 μ for the 1-mm pitch screw. Geared to the first encoder are two others which read whole turns. The configuration of conducting and insulating sectors on the disk is coded so that the output of a number of contact brushes fed to a transistorized translator produces a decimal number which changes in increments of 0.0005 mm as the screw is turned. A digital display mounted above the oscilloscope screen of the photoelectric setting device is energized by the translator and exhibits the comparator reading at any instant. When a setting has been made the readout button is pushed manually and the translator output is stored while it is being fed to an IBM 526 printing summary card punch, one digit at a time. The punch is programmed to operate column by column to read out storage, to skip other columns for spaces, or to duplicate still other columns from the previous card. In addition to the millimeter reading the punch records the settings of seven tap switches which are adjusted for each line to indicate grating order, intensity, line quality, etc. The line setting takes about two seconds, the tap switch adjustment zero to four seconds, and the readout one second, after which the operator can store the setting of the next line (the comparator can be advanced immediately after storage). The plate number and date are punched manually on the first card in the appropriate columns and are automatically duplicated on succeeding cards. Provision is made for stopping the card after the readout, if desired, for manually punching a note. About 2000 settings can be made per day.

While an essential feature of the system is the fact that the punched cards are immediately ready for processing in the computer, there are advantages to punched card comparator output even if no computer is to be used. Not having to write down the comparator readings by hand saves a surprising amount of time; about a factor of 5. Reading and transcribing errors are almost entirely eliminated. The fact that the reading is printed on the top of the card as well as punched makes it possible to check previous settings and revise them if necessary by inserting new cards, which is a considerable advantage over punched tape. Printed listings of the cards can readily be obtained using a standard accounting machine. On the other hand the investment is appreciable, about $6000 for the encoder and translator plus a monthly rental of $110 for the punch. Moreover, an appreciable effort is required for the installation and maintenance, so that the procedure is profitable only if a considerable volume of work is contemplated.

C. Computation

For a digital computer the solution of Eq. (2) is almost, but not quite, trivial. An IBM 650 computer has been used in the present work because this machine accepts punched card input and furnishes punched card output, both of which are advantageous for the present purpose over tapes. With this requirement the speed is limited not by the computation but by the rate at which cards can be fed in and punched out; about 120/min. There is thus no advantage to the use of a faster computer, say an IBM 704, and a 650 is inexpensive.*

The comparator output, one setting per card, is submitted in batches covering portions of the photographic plate. At the beginning of each batch, a card is inserted containing the wavelength, setting, and grating order of the line selected as the standard, the barometric pressure and temperature for correction to standard air, and the parameters of the grating—d, R, and $d \sin\alpha$. From this card the computer derives s_0 and then feeds in the data cards one at a time, computes, and punches out, one output card for each wavelength computed. The output also contains the vacuum wavenumber and

* Datex Corporation, Monrovia, California.

* The 650 is becoming obsolete and is being superseded by the IBM 1401, with four times the card feed rate and other advantages. The 1401 is also commonly used now for off-line conversion (punched cards to magnetic tape, etc.) for larger computers, so that use of a 704 is now possible.

all the miscellaneous information on the input card, such as intensity, notes, etc. There may be more than one output card per input card in case the grating order is not certain, provision being incorporated on the comparator tap switches to designate lower and upper limits.

The usual procedure is first to use the output cards in the original order of computation to obtain a printed listing, one tabular line per card, on an IBM 407 accounting machine. The listing is examined for misidentifications, impurity lines, wrong grating order in case a range of p is specified on the input, comparison lines, etc., and these entries indicated on the listing so that the corresponding cards can be removed from the computer output. The removal is usually done manually, although it is sometimes possible to remove certain cards by machine, e.g., those designated TH in the notes. Since the computer does not print the output on the top of the cards, as the summary punch does for the comparator output, the cards are put through an interpreter which supplies the printing corresponding to the punches. After the undesired cards are removed by thumbing through while noting the top printing, a new listing can be made. This is convenient for future reference since the computed wavelengths are still in the order in which they appear on the plates. The output cards are then put through a sorter which arranges them in order of wavelength, and a new listing is made. This listing contains all the measurements of the same spectrum line in different orders and different exposures as consecutive entries, so that they can readily be compared. It is usually more convenient to use this listing to find wavelengths computed for the wrong grating order because such cases do not appear in other orders. As the measuring program proceeds new computations can be merged with the old by machine and revised listings easily made. After all the measurements have been assembled and listed a best value for each wavelength is obtained by feeding the output cards back into the computer to form a weighted average. On these summary cards are punched by hand other data for the spectrum line such as hyperfine structure intervals, g values, etc., and a summary listing then made. This listing contains the working data for a term analysis, and the summary cards are suitable for machine methods of searching for constant differences and other analysis procedures by means of the computer. After a line has been classified, the terms involved in the transition can be added to the summary cards for use in further classification and for preparation of a final listing for publication by photographic reproduction. The advantage in flexibility of cards over tape can now be appreciated.

Some details of the computer program are given in Appendix A.*

* We are greatly indebted to Angelo Sandrin for the program.

D. Results

In order to use the grating equation it is first necessary to determine the parameters, R, d, and $d\sin\alpha$. The diameter of the circle and the angle of incidence can be determined directly by means of a steel tape, but the measurements are not reliable to better than 1 in 10^4. The method adopted was to measure with the comparator the separation between pairs of lines at various positions on the circle and to solve the resulting system of simultaneous equations. A unique set of parameters fitting many pairs of lines was not possible, due presumably to the residual errors in the circle, and a compromise set was adopted with a given value of R, a value of d for each of the two Bausch & Lomb gratings, and eight values of $d\sin\alpha$ corresponding to the proper combination of grating, slit position (23° or 53° angle of incidence), and orientation of the grating. (Since the error of run is different for the two gratings, the amount of roll is different, which changes the angle of incidence when the grating is turned on its axis to use the other side of the rulings.) Some commonly used sets of parameters are listed in Table II.

While it is necessary in principle to have only one standard line per plate it is clearly desirable to have more to serve as a check. Moreover, in establishing the parameters it is necessary to have a number of standards so that irregularities in the plateholder can be recognized. It was found that the thorium wavelengths of Meggers and Stanley[6] were much superior to previous standards for this purpose because the lines are sharper, more numerous, more uniform in intensity, and evidently more accurate. Over a 25-cm length of plate there were usually about a dozen of these standards, and the practice of measuring them all was adopted.

Some typical results obtained in the routine measurement of a set of plates exposed in a number of orders are listed in Table III. For most of the computations each plate was subdivided into several regions with a separate standard line for each; the additional effort in preparing extra parameter cards for the computer was negligible and some increase in accuracy resulted because of the

Table II. Grating Equation Parameters

Grating	Angle of incidence	Orientation	R (mm)	d (Å)	$d\sin\alpha$ (Å)
2	23°	A	9143.3	16666.89	6543.0
		B	9143.3	16666.89	6559.0
	53°	A	9143.3	16666.89	13312.0
		B	9143.3	16666.89	13328.0
3	23°	A	9143.3	16666.46	6530.0
	53°	B	9143.3	16666.46	13340.0

Table III. Thorium Wavelengths Measured by the Grating Equation

True	$p = 3$		$p = 4$		$p = 5$		$p = 6$		Wt. av
λ	λ	T − M[a]	λ	T − M	λ	T − M	λ	T − M	T − M[b]
3642·2487			Std	(0)	0.2480	7	0.2479	8	8(2)
3656·6936	0.6934	2	0.6938	−2	Std	(0)	0.6944	−8	−4(3)
3668·1396	0.1408	−12	0.1396	0			0.1402	−6	−6(2)
3669·9687	0.9694	−7					0.9687	0	−1(2)
3682·4861	Std	(0)	0.4869	−8	0.4879	−18	Std	(0)	−15(2)
3692·5661	0.5671	−10	0.5670	−9	0.5664	−3			−7(4)
3700·9780	0.9787	−7	0.9792	−12	Std	(0)	0.9803	−23	−15(3)
3711·3037	0.3034	3	0.3040	−3	0.3031	6	0.3051	−14	−3(4)
3719·4345	0.4335	10	0.4332	13	0.4326	19	0.4351	−6	8(4)
3727·9022	0.9023	−1	Std	(0)	0.9027	−5	0.9023	−1	−2(3)
3742·9231	Std	(0)	0.9219	12	0.9226	5	Std	(0)	8(2)
3752·5685	0.5686	−1	0.5641	44	0.5663 0.5693	22 −8	0.5665 0.5711	20 −26	7(6)
3762·9345	0.9324	21			0.9339	6	Std	(0)	12(2)
3771·3703	0.3711 0.3707	−8 −4			Std	(0)	0.3730	−27 4	−16(3)
3780·9663	0.9675	−12			0.9661	2	0.9659		0(3)
3785·5997	0.6013	−16	0.6001	−4	0.6014	−17	Std	(0)	−12(3)
3803·0750	Std	(0)	0.0747	3	0.0756	−6			−2(2)
3813·0674			Std	(0)	0.0691	−17	0.0666	8	−3(2)
3818·6855			0.6847	8	Std	(0)	Std	(0)	8(1)
								Av = ±7.2	

[a] True minus measured in 10^{-4} Å.

[b] (T − M) Weighted proportional to p, with (number of cases).

shorter distances between standard and unknown lines. A few cases in brackets refer to repeat computations on the same line obtained in overlapping regions. It should be emphasized that the measurements of Table III each represent one setting on one plate.

In evaluating the errors found in Table III it should be pointed out that the plate factor is 0.60 Å/mm at $p = 3$ and 0.29 at $p = 6$, while the setting error is not more than 0.001 mm, so that the precision would be expected to be in the fourth decimal place in wavelength. The actual errors are often somewhat larger than this and are believed to represent primarily irregularities in the plateholder.* The effect is, of course, reduced by averaging over a number of orders.

V. Wavelength Measurement with Polynomial Dispersion

Although the procedure based on a more precise circle using the grating equation was found to offer a considerable improvement in accuracy and speed in wavelength measurements, it still resulted in errors which sometimes were considerably larger than the statistical fluctuations corresponding to the precision. These systematic errors, due presumably to irregularities in the plateholder, could probably be reduced with a still more precise circle, with sufficient effort. With the availability of the thorium standards, however, the original motivation for the adoption of the grating equation procedure based on a single standard per plate had largely disappeared. It was, in fact, conceivable to consider going back to the old-fashioned procedure of using the thorium standards to establish a correction curve for wavelengths calculated not, of course, assuming linear dispersion but from the grating equation since it was nearly right. A manual correction procedure, however, would destroy much of the advantage of machine computation. An alternative method of computation was therefore sought.

One possible approach was to modify the parameters of the grating equation so as to give the best fit for each small region. This could be done automatically by the computer by furnishing the settings for four standards per plate, from which s_0, R, d, and $d \sin\alpha$ could be obtained by solving four simultaneous equations. This procedure would ensure that the equation was exact at four points on the plate instead of one, which should reduce the error at intermediate points. It would have the disadvantage that the solution would be sensitive to measurement errors in the positions of the standards, which might produce rather queer loops in the dispersion if the solution was forced to go through an erroneous point. Such errors would be less important if

* Nonuniform shrinkage of the photographic emulsion near the ends of the plate is another source of error, resulting in apparent wavelengths which are shifted toward the center of the plate. This effect is large for the first few millimeters near the ends and is observable as far as about 20 mm. Such cases have not been included in Table III.

Table IV. Thorium Wavelengths Measured by the Polynomial Method

True λ	$p = 3$ λ	$p = 3$ T − M[a]	$p = 4$ λ	$p = 4$ T − M	$p = 5$ λ	$p = 5$ T − M	$p = 6$ λ	$p = 6$ T − M	Wt. av T − M[b]
3642·2487	0.2490	−3					0.2487	0	−3(1)
3656·6936	0.6925	11					0.6936	0	11(1)
3668·1396	0.1404	−8					0.1396	0	−8(1)
3669·9687	0.9689	−2					0.9687	0	−2(1)
3682·4861	0.4857	4	0.4862	−1	0.4862	−1	0.4861	0	0(3)
3692·5661	0.5667	−6	0.5657	4	0.5657	4	0.5659	2	2(4)
3700·9780	0.9783	−3	0.9783	−3	0.9783	−3	0.9786	−6	4(4)
3711·3037	0.3033	4	0.3042	−5	0.3041	−4	0.3030	7	1(4)
3719·4345	0.4333	12	0.4337	8	0.4337	8	0.4344	1	6(4)
3727·9022	0.9025	−3	0.9025	−3	0.9026	−4	0.9027	−5	−3(4)
3742·9231	0.9238	−7	0.9232	−1			0.9228	3	0(3)
3752·5685	0.5694	−9	0.5685	0	0.5685 0.5686	0 −1	0.5686 0.5685	−1 0	−1(6)
3762·9345	0.9329	16			0.9340	5	0.9344	1	6(3)
3771·3703	0.3709	−6			0.3707	−4	0.3706	−3	−4(3)
3780·9663					0.9664	−1	0.9660	3	−1(2)
3785·5997					0.5996	1	0.5999	−2	−1(2)
3803·0750					0.0746	4	0.0750	0	0(2)
3813·0674					0.0680	−6			−6(1)
3818·6855					0.6852	3			3(1)
									Av = ±3.4

[a] True minus measured in 10^{-4} Å.

[b] Average (T − M) weighted proportional to p, with (number of cases).

a least-squares solution using all available standards on the plate could be devised. Since this appeared difficult in terms of the grating equation directly, various simpler analytical approximations to the grating equation were investigated. It was found that over a 25-cm range a simple third-degree polynomial $p\lambda = a_0 + a_1 s + a_2 s^2 + a_3 s^3$ reproduces the grating equation to within 0.0001 Å. By introducing more coefficients, therefore, it should be possible to account for irregularities in the circle. There is a practical limit to the power of the polynomial, set by the fact that a least-squares fit is desirable, which requires fewer coefficients than standards. After investigation a fourth-degree polynomial was adopted:

$$p\lambda = a_0 + a_1(s - s_0) + a_2(s - s_0)^2 + a_3(s - s_0)^3 + a_4(s - s_0)^4, \quad (3)$$

where $s_0 = (s_1 + s_n)/2$, the midpoint between the first and last standards. The introduction of s_0 reduces the magnitude of the variable and makes it significantly easier to determine the coefficients.

As an example of the results obtained by the polynomial computation the same measurements treated by the grating equation procedure and listed in Table III have been recomputed and are shown in Table IV.

Table V. Effect of Eliminating Large Deviations

True λ	A all lines λ	A T-M	B 1 eliminated λ	B T-M	C 2 eliminated λ	C T-M	D 3 eliminated λ	D T-M
3642·2487	0.2490	−3	0.2491	−4	0.2490	−3	0.2487	0
3656·6936	0.6925	11	0.6924	12	0.6925	11	—	—
3668·1396	0.1404	−8	0.1403	−7	0.1404	−8	0.1399	−3
3669·9687	0.9689	−2	0.9689	−2	0.9689	−2	0.9685	2
3682·4861	0.4857	4	0.4857	4	0.4857	4	0.4855	6
3692·5661	0.5667	−6	0.5668	−7	0.5667	−6	0.5667	−6
3700·9780	0.9783	−3	0.9785	−5	0.9782	−2	0.9783	−3
3711·3037	0.3033	4	0.3034	3	0.3030	7	0.3032	5
3719·4345	0.4333	12	0.4334	11	—	—	—	—
3727·9022	0.9025	−3	0.9024	−2	0.9021	1	0.9022	0
3742·9231	0.9238	−7	0.9234	−3	0.9232	−1	0.9231	0
3752·5685	0.5694	−9	0.5688	−3	0.5688	−3	0.5686	−1
3762·9345	0.9329	16	—	—	—	—	—	—
3771·3703	0.3709	−6	0.3701	2	0.3702	1	0.3703	0
		Av ±6.7		Av ± 5.0		Av ±4.1		Av ±2.4

It will be noted that the average error has been reduced by a factor of 2 and the maximum error greatly reduced.

Several details of the procedure should be mentioned. The fact that a number of standards are treated together reduces the effect of accidental errors but at the same time increases the chances of a mistake in identifying a standard or transcribing a standard wavelength. As a safety measure the program evaluates the error in fitting each standard to the polynomial. If any error is found to be larger than three times the average error the standard is discarded and a new polynomial is fitted to the remaining standards. This process is repeated if necessary by the program eliminating the largest error at each stage until no error is three times the average. This is always possible because if the number of standards is reduced to five the least-squares procedure degenerates to an exact fit for the five coefficients, as shown in the first case for $p = 6$, Table IV. It may happen, however, that the mistake is such that all the errors are large but comparatively uniform, in which case the safety test fails. Such cases are rare. The test has actually been found most useful in improving the fit by eliminating bad measurements, usually on weak standard lines. Poor measurements sometimes have a surprisingly large effect in increasing the average error. This is illustrated in Table V in which the lines showing the largest deviations in Table IV, $p = 3$, are successively eliminated. Figure 7 is a plot of the deviations and shows how a large deviation forces the neighboring standards away from the zero axis. It is, however, necessary to exercise restraint in the elimination process in that use of fewer standards will lead to a smaller average deviation for the standards but may produce a polynomial with large coefficients for the high-degree terms, leading to an erratic dispersion in between the standards.

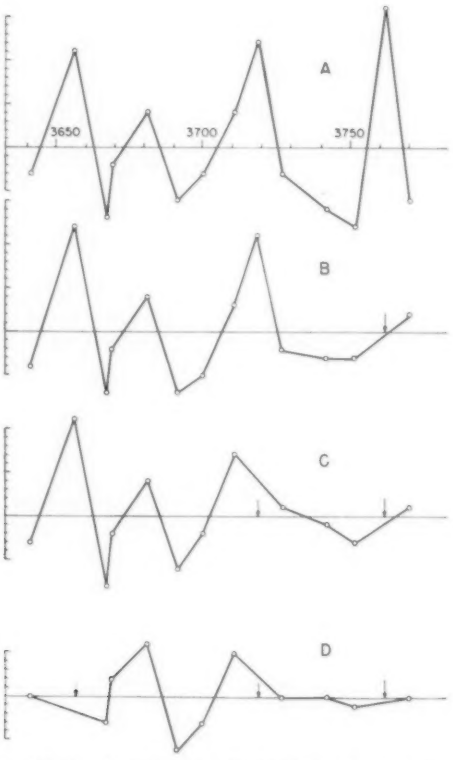

Fig. 7. Effect of successive eliminations of poor standards. Data for Table V.

Table VI. Effect of Correction for Nonstandard Atmosphere

True λ	p	With correction M	With correction T − M	Without correction M	Without correction T − M
4178·0598	6	0.0603	−5	0.0605	−7
5017·2545	5	0.2536	9	0.2531	14
3592·7788	7	0.7794	−6	0.7797	−9
4193·0165	6	0.0160	5	0.0157	8
3598·1196	7	0.1200	−4	0.1203	−7
5049·7959	5	0.7951	8	0.7945	14
4214·8283	6	0.8283	0	0.8282	1
3615·1324	7	0.1328	−4	0.1331	−7
3622·7951	7	0.7950	1	0.7949	2
			Av ±4.7		Av ±7.7

The correction for nonstandard atmosphere is more involved than for the grating equation procedure because the standards to be fitted by the polynomial will, in general, belong to a number of different grating orders and formula (A5),* based on the differential shift of a pair of lines, is not applicable. Instead, the standard wavelengths are first converted to the actual wavelengths in laboratory air by means of (A4)* and then fitted to the polynomial. The unknown wavelengths computed from the polynomial, therefore, are based on laboratory air and are converted to standard air by $(A4)^{-1}$.* The change in wavelength in going from standard air to laboratory air is usually in the second decimal place, but the error introduced by assuming that the standards in laboratory air have the wavelengths specified for standard air is much less, being of the order of the differential correction (A5).* This error is not always directly demonstrable because the least-squares procedure tries to do the best it can to fit the standard wavelengths provided. The effect of omitting the correction is shown in Table VI for a set of standards which is a mixture of $p = 5, 6, 7$, showing a significant increase in all the deviations but especially for the two with $p = 5$.

In evaluating the over-all accuracy of the procedure there are several characteristics of the concave grating spectrograph which should be mentioned. It is inherently more difficult to produce a uniformly ruled surface on a concave grating than on a plane grating,

* Appendix A.

and some areas of the ruling may appear brighter than adjacent areas. The relative brightness of different areas usually depends on wavelength, so that for a given $p\lambda$ the effective area varies with p. Since the line definition of an imperfect grating is necessarily imperfect, the line contour varies with p. The effect, then, is somewhat similar to the effect of a nonstandard atmosphere, but the algebraic sign and magnitude depend on the peculiarities of the grating. A related effect of an imperfect line contour is that the peak position appears shifted on a heavy exposure, so that the deviations show a dependence on intensity (Table I).

Even for a perfect grating there are errors which can arise in comparing lines at different vertical positions on the plate due to line tilt. The irregularities in the plateholder curvature will not in general be the same for the upper and lower rails, which will introduce an irregular skewness to the plate. This produces a line tilt which varies along the plate and causes a variable shift of the two spectra being compared. The effect can be eliminated by readjusting the plate on the comparator at suitable intervals, if necessary. Since the error with the present plateholder adjustment is small it has been considered more feasible for our purposes to ignore the shift, and expect that it will be compensated for in averaging measurements made in a number of orders.

An additional shift is introduced between different exposures due to line curvature. For adjacent exposures near the middle of the lines the effect is slight, but for exposures 1 cm or so apart the shift may approach 10 μ. It is a great convenience to have identical reference exposures symmetrically placed about the midpoint to assist in aligning the plate on the comparator so as to minimize the effect.

As an illustration of the capabilities of the polynomial procedure, recent experience in measuring lines in the spectrum of protactinium may be cited. Plates exposed in a number of grating orders were measured at an average rate of 1000 lines per day for a period of 2.5 months, yielding about 10,000 different lines when averaged. These measurements were made by a spectroscopist without previous experience in grating wavelength determination. The accuracy may be judged by the constant differences shown in Table VII, which are believed to be transitions to the two lowest levels of Pa I. The average deviation in the constant difference of ± 0.008 cm^{-1} corresponds to about ± 0.0013 Å.

Table VII. Constant Differences in Pa I

σ_i	σ_j	$\Delta\sigma$	$\overline{\Delta\sigma} - \Delta\sigma$
27889.588 cm^{-1}	27064.171 cm^{-1}	825.417 cm^{-1}	0.016 cm^{-1}
24582.775	23757.351	825.424	0.009
26818.893	25993.462	825.431	0.002
25104.469	24279.037	825.432	0.001
27638.034	26812.601	825.433	0.000
25586.535	24761.097	825.438	−0.005
27078.811	26253.355	825.456	−0.023
		Av 825.433	±0.008

We are greatly indebted to Herbert Ostrander for the design of the improved plateholder, and to Joseph A. Cate for the adjustment procedure. The computer programs are due to Angelo Sandrin, whose help has been invaluable We should like to thank A. Giacchetti for permission to quote his Pa measurements.

Appendix A. Computer Program for Grating Equation

The IBM 650 computer uses for storage a magnetic drum having 2000 locations each with 10 decimal digits. Most programs involving arithmetic operations are written in what is known as floating point, in which the last two digits of a given word (location) are used as exponent for the power of ten by which the first eight digits are to be multiplied This gives a range of 10^{100} for numerical data and removes the difficulty of handling large and small numbers without loss of significant figures. The result, however, of a succession of operations, e.g., a series expansion for $\sin\beta$, is that the eighth significant figure is in doubt because of an accumulation of rounding errors. This is awkward for the present purpose because the experimental accuracy attainable for the wavelengths in favorable cases is a few units in the eighth place, and it is clearly undesirable to sacrifice any of this accuracy because of the computation. Two solutions are available, double precision and fixed point operation. In the former method a given number is divided between two locations with the appropriate exponent in each, making a total of 16 digits available. Operations such as multiplication of two numbers $A = a_1 + a_2$ and $B = b_1 + b_2$ are more involved, however, because of the separate products which must be formed and summed, and the time required becomes a serious limitation for mass production. In fixed point operation the exponent is eliminated and all 10 digits of a word can be used for each number. The usual objection that significant figures may be lost does not apply to the present case where the quantities are always in the same range, and two extra digits become available. The only requirement is that all data must be presented in the prescribed columns with the decimal point always in the same place and a zero entered for a missing digit.

At the beginning of each group of data cards is placed a transfer card which clears the drum locations containing the previous parameters. The next card is the new parameter card used to compute:

$$s_0 = -s + R \sin^{-1}[(1/d)(p\lambda - d\sin\alpha)]. \qquad (A1)$$

The usual procedure for the evaluation of $\sin^{-1} x$ is by means of a Hastings[11] approximation:

Table A1. Coefficients of Hastings Polynomials

a_i	$\sin^{-1}x$				$\sin x$			
a_0	1.570	796	321	8				
a_1	−0.214	601	396	4	0.999	999	994	7
a_2	0.089	036	508	3				
a_3	−0.050	648	632	2	−0.166	666	567	0
a_4	0.032	796	693	7				
a_5	−0.021	224	217	6	0.008	333	025	2
a_6	0.011	631	517	6				
a_7	−0.004	355	139	1	−0.000	198	074	1
a_8	0.000	781	921	9				
a_9					0.000	002	601	9

$$\sin^{-1}x = \frac{\pi}{2} - \sqrt{1-x}\,[a_0 + a_1x + a_2x^2 + \ldots + a_nx^n]. \tag{A2}$$

The number of terms included in the polynomial depends on the accuracy required, and Hastings lists sets of coefficients a_i for polynomials of various degrees. Since the best of these was not quite adequate, the coefficients of the next higher degree polynomial were derived by the standard procedure and are listed in Table A1. The maximum error for this approximation is 10^{-9}. The table includes for convenience the coefficients of $\sin x = \sum a_i x^i$, taken from Hastings.[11]

The computer then feeds in data cards and computes λ from Eq. (2) for each p from p_1 to p_2, the lower and upper limits specified by the tap switch settings at the time the line position is punched. In addition the vacuum wavenumber $\sigma = 10^8/n\lambda$ is computed, where n is the index of refraction of standard air given by Edlén's dispersion formula.[8]

$$n = 1.000064328 + \frac{2{,}949{,}810}{14{,}600{,}000{,}000 - (10^{16}/\lambda^2} + \frac{25{,}540}{4{,}100{,}000{,}000 - (10^{16}/\lambda^2)}. \tag{A3}$$

The published wavelengths of the lines suitable as standards are quoted for standard air (15°C, 760-mm Hg barometric pressure), but laboratory air at Argonne is appreciably different (24°C and on the average 740 mm). The actual wavelength is given by

$$\lambda(T,B) = \lambda(15{,}760)\,\frac{n(15{,}760)}{n(T,B)} = \frac{\lambda(15{,}760)}{n(15{,}760)}\left\{1 - [n(15{,}760) - 1]\left[\frac{B}{760}\right]\left[\frac{273+15}{273+T}\right]\right\}. \tag{A4}$$

Since n is of the order of 1.0003 the change in wavelength is several hundredths of an angstrom. This change is not important if the wavelength of the standard is near that of the unknown line since the change will be about the same for both lines. Hence, use of the standard wavelength specified for standard air will then automatically provide unknown wavelengths appropriate to standard air. If the standard and unknown λ's belong to different grating orders, however, the differential shift will be appreciable. In this case the program corrects the wavelength calculated from Eq. (2) according to the formula given by Edlén[8]:

$$\Delta\lambda = \lambda(n - n_{\mathrm{std}\lambda})\left[\frac{B}{760}\cdot\frac{273+15}{273+T} - 1\right]. \tag{A5}$$

The correction is usually in the fourth decimal place in angstroms and, within our experimental error, appears to be given adequately by the above expression.

Appendix B. Computer Program for Polynomial Dispersion

The polynomial computation can be performed satisfactorily by fixed-point operation once the coefficients have been determined. In order to solve the normal equations in the least-squares procedure, however, it is necessary to carry a large number of significant figures. For the 650 it was necessary to resort to double precision operation. For variable word length machines use of 15 digits is recommended for the normal equations.

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ERRATUM

D. J. Bradley, "Improved Silver Films for Multiple-Beam Interferometry", Appl. Opt. **2,** 539 (May 1963)

First three lines at top of right hand side should read "duced by the focusing properties of the boat filament, and a preliminary calibration is necessary. On passing a current of 150 A through the filament, most of the silver goes off in less than 5"

Meeting Reports *continued from page 706*

Spring Meeting of the Optical Society of America, Robert Meyer Hotel, Jacksonville, Florida, 25–27 March 1963

Reported by Dennis C. Marquis, Pan American World Airways/ Guided Missiles Range Division

The first meeting of the Optical Society to be held in the South proved to be quite successful, with a total registration of about 500 persons. The primary theme of the meeting was optics in the space age; sessions on spectroscopy and fiber optics, radiometry, color and photometry, geometrical optics and lens design, spectra, thin films, vision, and photography were also presented. A wide variety of optical maser topics were covered in two separate sessions, including papers on materials, laser emission characteristics, modulation techniques, and system applications. Invited papers on atomic-emission spectroscopy, the Luneburg theory of binocular vision, optical masers, and space optics were presented by Curtis Humphreys, Thorne Shipley, Oliver S. Heavens, and James Kupperian, respectively. The 1963 Tillyer Medal was presented to Clarence Graham *Columbia* at the banquet by the past recipient, Glenn Fry. Graham also presented an invited paper on aspects of real and apparent visual movement.

One-hundred contributed papers filled the remainder of the three-day meeting, with a new and well-received innovation in the form of a panel discussion on new optical materials. Members of the panel included Frank Cooke, Walter Siegmund, William Wolfe, Lawrence Dunkleman, Richard Tousey, and A. F. Turner. Stanley S. Ballard was the moderator of the session, and, after brief presentations by each panel member, a lively discussion ensued. Even though the panel discussion was held during the afternoon of the last day, the attendance was excellent, attesting to the interest in this type of format.

On Tuesday afternoon, Major John Young from the Atlantic Missile Range presented slides depicting the mission and instrumentation used on the Range. This was followed by an excellent movie which showed some successes and failures in the U.S. missile program.

The Edgar D. Tillyer Medal for 1963 of the Optical Society of America is awarded to Clarence H. Graham *Columbia University* (right) by 1963 OSA President Stanley S. Ballard during the OSA Spring Meeting in Jacksonville, Florida.

The banquet speaker was to have been astronaut M. Scott Carpenter, but a last-minute commitment prevented him from speaking. Robert Voast, the assistant director of the NASA Manned Spacecraft Center presented Carpenter's extremely interesting paper, "Observations from Space." The talk was supplemented by excellent color slides and a movie made during Carpenter's orbital flight. Total attendance at the banquet was 467, which represents one of the highest ratios of banquet attendance to total registration in OSA history.

On Thursday, 190 OSA members took part in an all-day tour of Cape Canaveral. Escort officers boarded the air-conditioned chartered buses at the gates of Cape Canaveral and directed a 90-minute driving tour of the Cape. At the conclusion of the tour, the buses were parked about two miles from the Saturn launch pad, and the members lounged in the Florida sun (some carried effects of this proudly up North) until the mighty Saturn gave a spectacular display in a very successful flight.

Third Quantitative Spectroscopy and the Special Problems of the Space Sciences Conference, 20–22 March 1963, California Institute of Technology

Reported by Shirleigh Silverman, Office of Naval Research

The second conference on Quantitative Spectroscopy to be held at Caltech broadened its subject matter and the title of the conference, Quantitative Spectroscopy and the Special Problems of the Space Sciences, showed the impact of the space age on spectroscopy. The impact was noted in other ways, too, especially in the much enlarged registration list, as compared to that of three years ago. The meeting was under the able direction of S. S. Penner *Caltech* and 23 papers were run during five sessions. Since the chairman assiduously avoided parallel sessions, it was possible to attend everything one wanted to hear, and the pace seemed so leisurely and comfortable that one was scarcely aware of the large variety of topics covered and of the firmness with which the schedule was adhered to.

The absence of P. Swings *Liège* due to illness, M. Migeotte *Liège*, and G. Herzberg *NRC-Ottawa*, both for unavoidable reasons, left large gaps, as did the last-minute loss of W. S. Benedict *Johns Hopkins*, but the chairman was skillfully able to rearrange the schedule. The first session, on the absolute intensities measurements in heated gases, was started off appropriately enough by R. B. King of the host institution, who described the travails of the elegant experiments he and his students have carried out on absolute intensities on atomic beams. There followed the definitive work of H. N. Olson *Northrup* on very stable electric arcs, the work of the Avco and Cornell-Aero groups on shock tubes, and Kolb *NRL* on high-temperature plasmas. The second session was devoted to experimental and theoretical studies of absolute intensities. Vodar *Bellevue* presented a comprehensive *revue* of the lively group working there of pressure induced transitions, and was followed by Polanyi *Toronto* who shed some much needed light on chemiluminescent radiation from reacting gases; Layzer *Harvard* gave emphasis to problems of astrophysical importance in a discussion of absolute intensities of neutral and ionized atoms. Ginsberg and the writer filled in for W. S. Benedict, who was unexpectedly called home, with short papers on the rotational spectrum of water, and wing absorption of CO_2 in the 4-μ region, respectively. Ginsberg's results on H_2O confirm theory very nicely. The third session began with Rank *Penn State* presenting what must be the most beautifully determined measurements of spectral line profile in existence; he was followed by Welsh *Toronto*, who picked up the theme of Vodar from the previous day and reviewed the work of the Toronto group on intensities and

continued on page 739

Selection of Multilayer Dielectric Coatings for Fabry-Perot Interferometry

Sumner P. Davis

The parameters appropriate to selection of multilayer dielectric coatings for Fabry-Perot interferometry in the ultraviolet and visible regions of the spectrum are discussed. A representative example is given.

I. Introduction

High-resolution work in optical spectroscopy is becoming increasingly important as more accurate measurements of hyperfine structures and line shapes become necessary. While the marked improvement in diffraction gratings in recent years[1,2] has partially fulfilled the increased demands, the Fabry-Perot interferometer is still unsurpassed for its resolution and luminosity in many regions of the spectrum.[3] Recent work at Berkeley in the field of optical hyperfine structure, using light sources of limited intensities, has compelled a re-examination of the usefulness of the Fabry-Perot interferometer and available reflecting coatings, in order to utilize fully its advantages in the visible and near ultraviolet regions of the spectrum. The usefulness of coatings of silver and aluminum has been thoroughly investigated by others.[4,5] The decision to concentrate on dielectric coatings came about because of their relatively small absorption losses and developments in their technology.

II. Fundamental Considerations

The general theory and practical applications of the Fabry-Perot interferometer have been thoroughly discussed by Meissner.[6] There have been many more recent developments in theory and in specialized applications, but only those references will be cited which have a particular use here. Three properties or parameters are significant for high-resolution work: the free-spectral range, the instrumental width, and the transmission factor.

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The figures in this article have been reproduced larger than is usual for this journal since they are designed to be used in calculations, rather than simply to present information.

A. Basic Equations

The instrumental function of a perfect Fabry-Perot interferometer with a monochromatic source of radiation is the Airy equation

$$\tau_R(\lambda) = \frac{1}{(1 + A/T)^2} \times \frac{1}{1 + (4R\sin^2\pi\Delta/\lambda)/(1 - R)^2},$$

where A is the absorption coefficient, T the transmission coefficient, and R the reflection coefficient; the path difference $\Delta = 2t\cos\theta$ in vacuum. Further, the equation $m\lambda = 2t\cos\theta$ expresses the relationship between the order m, the wavelength λ, the spacer thickness t, and the angle of observation θ of the transmitted radiation.

B. Free-Spectral Range

The free-spectral range, or spectrum interval free from overlapping, is given approximately by $F_\sigma = 1/(2t)$. For example, an interferometer with a 1-cm spacer has a free spectral range of 0.5 cm^{-1} (0.125 Å at 5000 Å).

C. Instrumental Width

The instrumental width is often called the resolving limit, or wavenumber difference between two monochromatic radiation sources, whose wavenumbers differ by the instrumental width at half-maximum transmission. The value of this width is given approximately by

$$\Delta\sigma = \frac{1 - R}{\pi\sqrt{R}} \times \frac{1}{2t}$$

or

$$\Delta\sigma = \frac{1 - R}{\pi\sqrt{R}} \times F_\sigma.$$

The quantity $\pi\sqrt{R}/(1 - R)$ is denoted by N_R, and is called the equivalent number of interfering beams, or *finesse*, by analogy with the often used formula for the

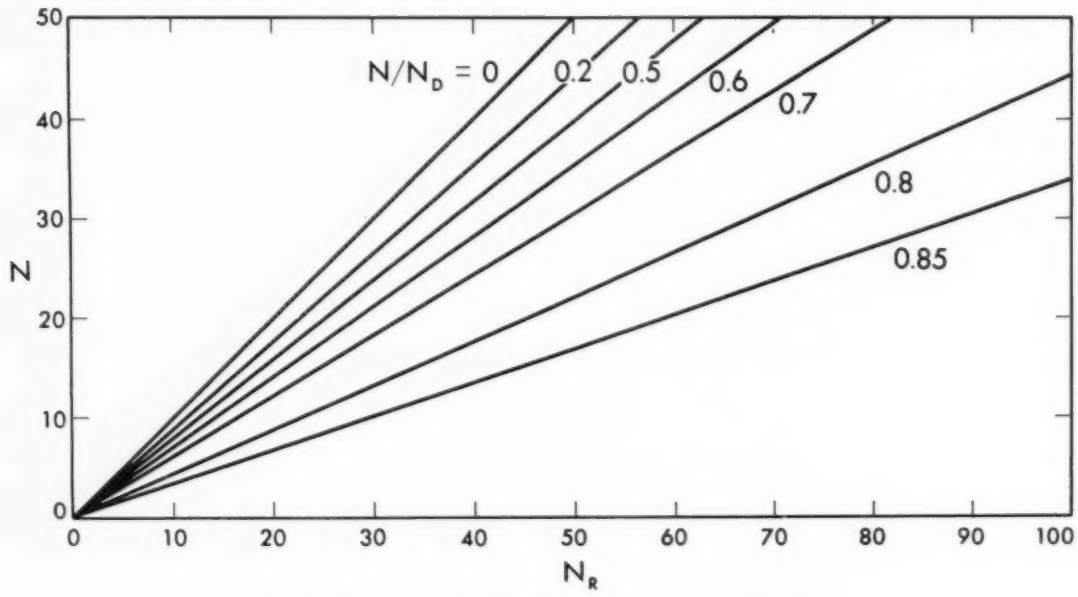

Fig. 1. Finesse vs reflecting finesse, as a function of N/N_D.

resolving power of a spectroscopic instrument $R = mN$. The resolving limit is then $1/N_R$ times the free-spectral range. A typical value of N_R is 20, so that with a 1-cm spacer, the free-spectral range is 0.5 cm^{-1} and the resolving limit is 0.025 cm^{-1} (a resolving power of 800,000 at 5000 Å).

In the case of an actual interferometer with plates not perfectly flat, the above result is modified. The relationships are complex, but have been studied in detail.[7] It is customary to call N the finesse of the interferometer, N_R the finesse owing to the reflection coefficient R, and N_D the limiting finesse owing to the flatness of the plates. If the plates are flat to λ/k, then the limiting finesse $N_D = k/2$. Typical values of N_D run from 10–100.

D. Transmission

The maximum transmission of the interferometer as given by the Airy function is $\tau_R = 1/(1 + A/T)^2$. It differs from unity because the coatings have an absorption coefficient $A = 1 - R - T$. This result must be modified because of the lack of perfect flatness of the interferometer plates.[7] The multiplying factor is called τ_D, making the total transmission $\tau = \tau_R \times \tau_D$.

III. Selection of Parameters

A. General Considerations

Usually the problem at hand is the resolution or separation of some particular lines. The line sharpness and separation fix the upper limit on the allowable instrumental width. It might appear that the only problem is that of the choice of a sufficiently large reflection coefficient R, to give a large value of reflecting finesse, and then to select the spacer thickness large enough to permit resolution of the lines in question. Practically speaking, this solution is unsatisfactory. If the reflectance of the coatings is too high, the light transmission becomes so low as to render the interferometer nearly useless. Also, because of its relatively small free-spectral range, the interferometer must be used in conjunction with a narrow pass filter or auxiliary spectrograph, in order to eliminate blending with other lines emitted by the light source. At the very least, the auxiliary spectrograph must have sufficient resolution and dispersion to separate one free-spectral range of the interferometer. Even this is not sufficient in many cases, since a hyperfine structure pattern is often wider than a free-spectral range, yet has some very closely spaced components. In the past, it has been the practice to allow some overlapping of interferometer orders, and to choose spacer thicknesses of just the proper sizes to result in nonblending of lines. The subsequent unscrambling of patterns often resulted in ambiguous interpretations.

With the recent development of large, well-ruled diffraction gratings, another solution has become practical. The high resolution and dispersion of stigmatic plane grating spectrographs make it possible to resolve the "gross" hyperfine structure with the grating alone, while leaving the Fabry-Perot interferometer the task of resolving the more closely spaced lines.

We can proceed in the following way: first choose the free-spectral range as small as possible consistent with the resolution and dispersion of the auxiliary spectrograph; select the minimum reflectance of the coatings

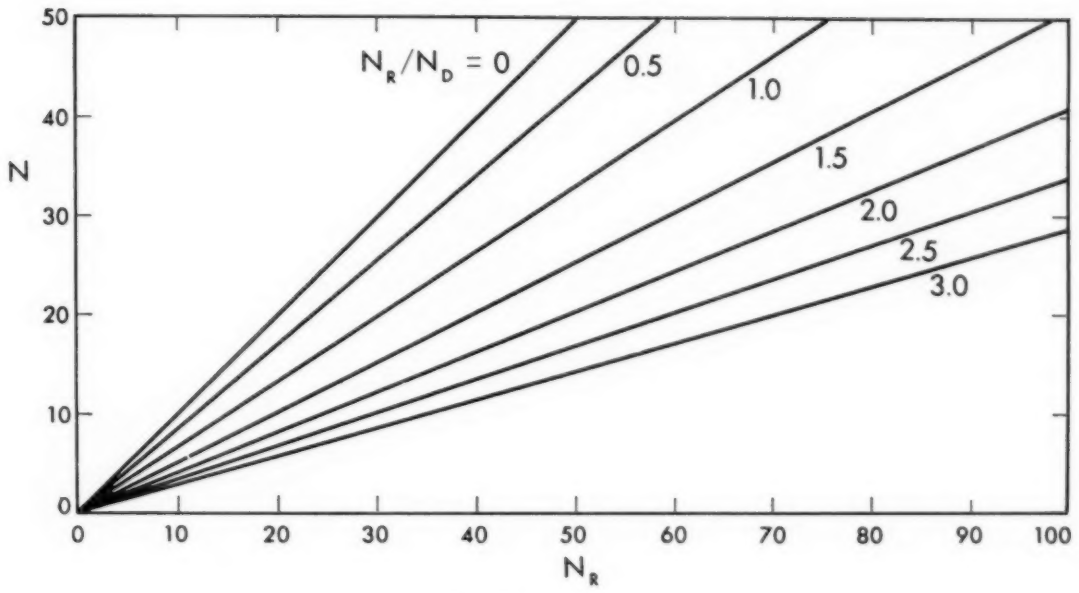

Fig. 2. Finesse vs reflecting finesse, as a function of N_R/N_D.

which will ensure a small enough instrumental width to resolve the closest spaced lines in question; determine the transmission of the interferometer, to ascertain if the experiment is still feasible. Naturally, since these considerations are interrelated, it is often necessary to make some compromises, which are best worked out by experience.

B. Choosing the Free-Spectral Range

Let us consider that the Fabry-Perot rings are focused on the slit of a stigmatic spectrograph. Some minimum length along each ring is necessary for measurement; this length is chosen as the slit-width of the auxiliary spectrograph. Assume that this length is x mm. Also, assume that the plate factor of the spectrograph is y cm^{-1}/mm. Then, the smallest free-spectral range tolerable with no overlapping is the product xy cm^{-1}. A representative example follows: slit-width 0.200 mm, plate factor 1.50 cm^{-1}/mm, minimum free-spectral range 0.300 cm^{-1}, corresponding to a spacer thickness of 16.7 mm. Of course, if the total width of the hyperfine structure pattern is less than this figure, the free-spectral range can be made correspondingly smaller.

C. Choosing the Reflection Coefficient *R* (the Instrumental Width)

The minimum free-spectral range is now fixed. If we assume that the problem at hand requires that the instrumental width be less than a fixed amount $\Delta\sigma$, the finesse is fixed at $N = F_\sigma/\Delta\sigma$. The appropriate value of reflection coefficient R to produce the required finesse N is found as follows.

First find the ratio N/N_D (see Sec. IIC), and then refer to Fig. 1, which presents graphically[2,7] the relationship between finesse N, and the reflecting finesse N_R. It is possible to have $N = N_R$ only for perfectly flat plates ($N/N_D = 0$). The scale on the ordinate is chosen to be representative of present possibilities. The upper limit is set by the usual operating conditions in the laboratory, since it is very difficult to utilize a finesse greater than 50, simply because the operating conditions are too stringent with respect to distortion of the plates in their holder, temperature, and pressure. (Figure 2 presents the same relationship, but as a function of N_R/N_D. This graph is useful when N_R is known, and N is to be determined. See Sec. IV.)

To find the reflection coefficient R, refer to Fig. 3, which is a plot of the relationship R vs $\pi\sqrt{R}/(1-R)$. Once the value of reflection coefficient has been chosen, the proper dielectric coating must be selected.

D. Choosing Dielectric Coatings

Much has been written about dielectric coatings for Fabry-Perot interferometers.[8-10] The usual practice is to deposit alternate quarter-wave layers of high- and low-index dielectric materials until the desired reflectance is obtained. The high-index material generally is the more durable, and constitutes both the first and last layers. The reflection coefficient can be computed from the following equation:

$$R = (n_H{}^{2s+2} - n_0 n_L{}^{2s})^2/(n_H{}^{2s+2} + n_0 n_L{}^{2s})^2,$$

where n_H, n_L, and n_0 are the indices of the high index, low index, and substrate materials. The total number of layers in the film is $(2s + 1)$. Conversely,

Table I. Dielectric Coating Materials

Material	Refractive index	Short wavelength limit of transparency (Å)	Loss in a multilayer stack (%)
Cryolite	1.35–1.39	2000	—
ZnS	2.30	4000	0–1
Sb_2O_3	2.1	2900	1–2
PbF_2	1.8	3500	0–1
	1.9	3000	1–2
	2.1	2500	2–5
	2.2	2400	3–10

knowing the value of R desired, the required number of layers can be calculated.

The choice of dielectric materials is somewhat restricted in Fabry-Perot interferometry for practical reasons. The films must be relatively durable under conditions of fairly frequent handling and exposure, and they must be removable without damage to the plates. The materials we have found most useful, together with some of their properties, are listed in Table I. More details are given in the references.[9–11] The losses given in the last column represent those due to absorption, scattering in the films, and surface roughness of the substrate. The figures can only be approximate owing to variations in coating techniques and substrate surfaces. As an example, a 5-layer stack of ZnS and cryolite at 5000 Å has a peak reflectance of about 87%, with losses between 0 and 1 %, and a reflecting finesse of about 23.

E. Determination of Transmission

The final consideration is the transmission of the Fabry-Perot interferometer. The transmission is the product of two factors: one, the maximum of the Airy equation $\tau_R = 1/(1 + A/T)^2$, and the other, a function resulting from the lack of perfect flatness of the plates.[7]

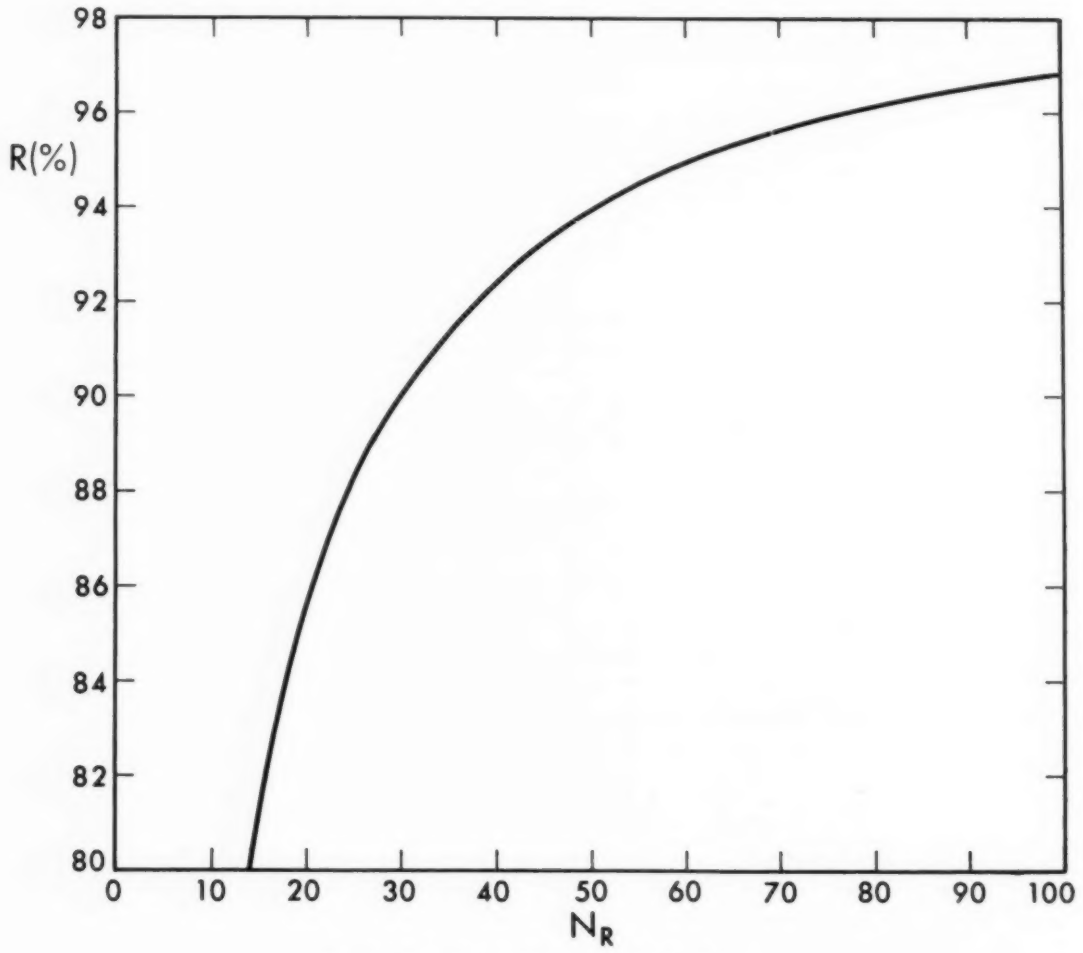

Fig. 3. Reflection coefficient vs reflecting finesse.

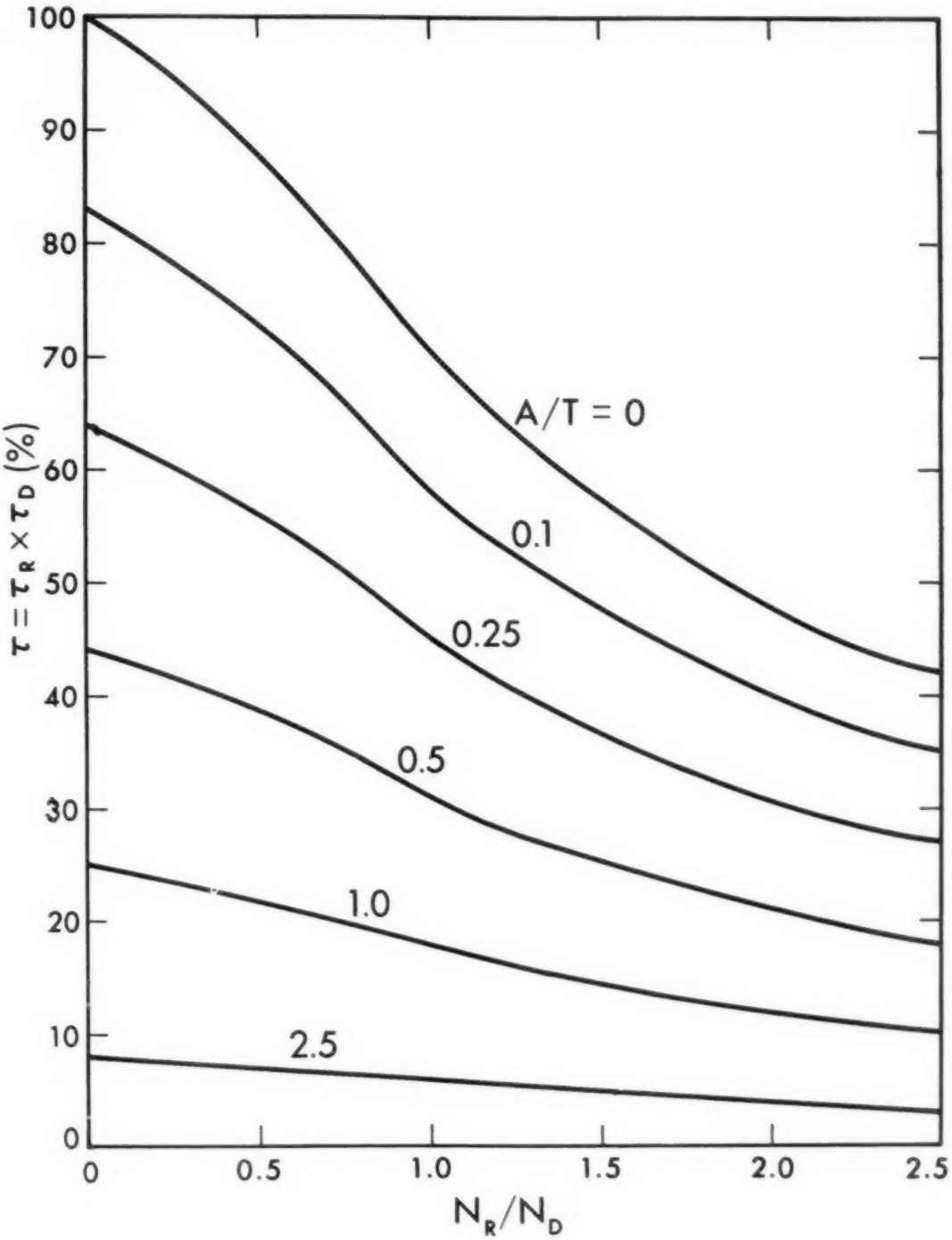

Fig. 4. Transmission of a Fabry-Perot interferometer.

The product of these two factors is graphically presented in Fig. 4, where the transmission is plotted as a function of N_R/N_D, for different values of the ratio A/T. For perfectly flat plates and no absorption losses in the film, the transmission is 100%, signifying that the only function of the interferometer in this case is to cut off light not at the correct angles, without a reduction in the maximum of the transmitted light.

IV. Illustrative Example

Suppose that it is desired to examine the structure of the 2537 Å line of mercury, which has a total width of approximately 0.740 cm^{-1}, and an individual line-width of about 0.035 cm^{-1}. The auxiliary spectrograph to be used has a plate factor of 3.5 cm^{-1}/mm (0.23 Å/mm at 2537 Å). The minimum slit-width (length of Fabry-Perot ring needed for measurement) is 0.2 mm. The minimum allowable free-spectral range is then calculated as F_s = (slit-width) × (plate factor) = 0.7 cm^{-1}. The spacer thickness is $t = 1/(2F_s) = 7.1$ mm. The required finesse to make the instrumental width equal to the line-width is N = (free-spectral range)/(line-width) = 20. To find the reflecting finesse, it is necessary to know the limiting finesse of the interferometer plates. A representative value is $N_D = 25$ at 2537 Å (plates flat to $\lambda/100$ in the green). Reference to Fig. 1 for $N = 20$ and $N/N_D = 0.8$ yields $N_R = 45$. From Fig. 3, it is found that a reflection coefficient of about 93% is required. A calculation for a 9-layer film of PbF_2 and cryolite (index 1.39 from Table I) on a substrate of fused silica (index 1.52) shows that the theoretical reflection coefficient R is 95%. Let us assume that the losses in the film are about 3%, resulting in a transmission of 2%, and a ratio $A/T = 1.5$. The curves in Fig. 4 show that the transmission of the interferometer is about 8%.

This example is an idealized one, and the exact figures must not be taken too literally. There are wide variations from coating to coating in the fabrication of dielectric films, especially in the ultraviolet region of the spectrum. Often the maximum reflectance does not reach the calculated value, owing to inaccuracies in thicknesses of the individual layers in the stack. Also, the calculation is based on the assumption of non-absorbing films. With absorption and other losses present, it must be regarded as an approximation. The general principles are nevertheless applicable. Specifically, to reach a reflectance of 95% at 2537 Å, it is necessary to use an 11-layer instead of a 9-layer film, as

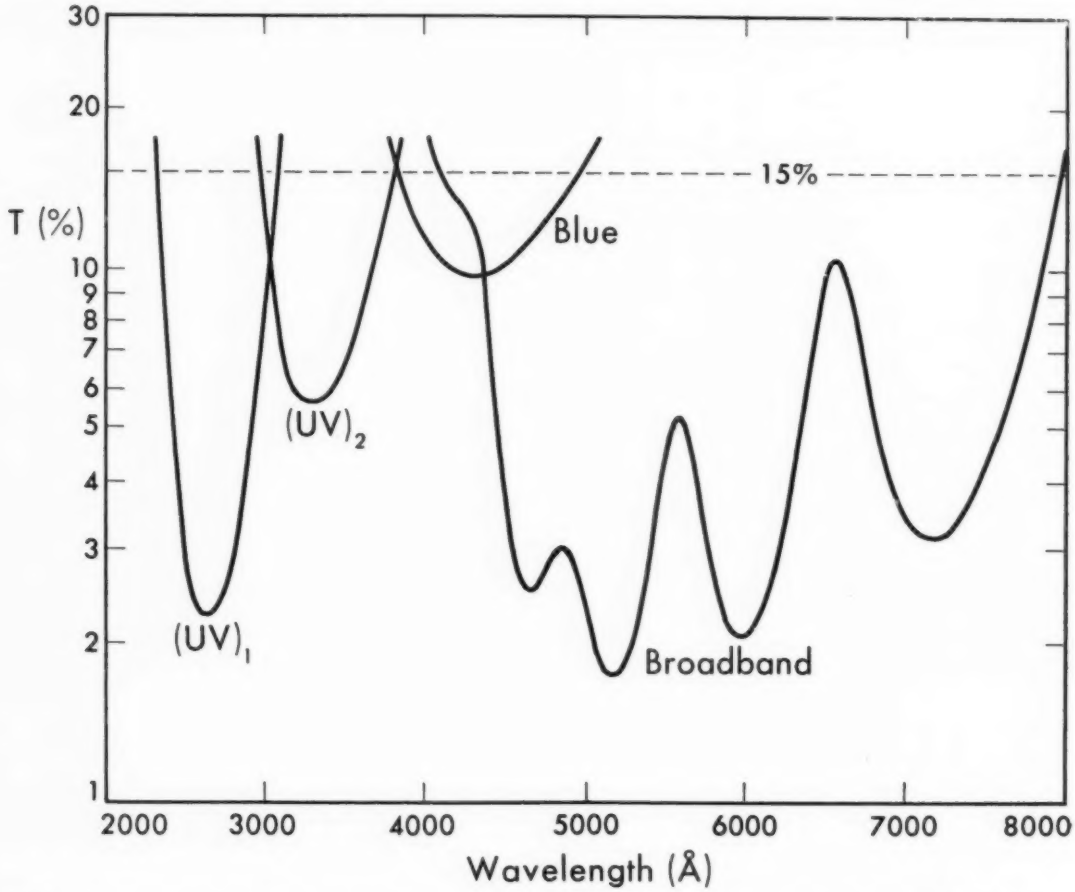

Fig. 5. Representative multilayer dielectric coatings for Fabry-Perot interferometry. $(uv)_1$, 11-layer PbF_2 and cryolite. $(uv)_2$, 7-layer Sb_2O_3 and cryolite. Blue, 5-layer ZnS and cryolite. Broadband, 15-layer ZnS and cryolite.

Fig. 6. Interferogram of mercury 2537 Å, taken under conditions outlined in the illustrative example in the text (negative and positive prints).

is shown in Fig. 5. All the curves presented in this figure are transmission curves (the usual laboratory instrument measures transmitted rather than reflected light); absorption losses must be estimated in order to obtain the reflectance. They are representative curves of films practically obtainable. Where the losses are small, the experimental curves closely approach the theoretical ones, as in the case of the "Blue" coating.

The interferogram reproduced in Fig. 6 accurately represents the figures of the example, and was taken with the 11-layer film labeled $(uv)_1$ in Fig. 5.

In practice, a dielectric coating may already be at hand, and the problem is then one of determining the finesse, given the transmission of the coating. The procedure is the reverse of that given in the example with the exception that Fig. 2 is used instead of Fig. 1, since N_R and N_D are known and N is to be determined.

V. General Remarks

The treatment given here is not exhaustive, and presents only a small part of the theoretical knowledge and technical lore of dielectric films and interferometers. Many other conclusions can be drawn about the uses of dielectric films, and many properties have not been mentioned. The aim has been to present those facets worthy of foremost consideration when planning the use of Fabry-Perot interferometers.

This work was supported in part by a grant from the National Science Foundation. The expert technical work of Josef Cayot in fabricating coatings is gratefully acknowledged.

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Applied Optics BOOKS

Books for review should be submitted to the Managing Editor APPLIED OPTICS, 1155 16th St., N.W., Washington 6, DC.

On the Broadening and Shift of Spectra Lines in the Plasma of a Gaseous Discharge. By M. A. Mazing. (Part 2 of an authorized translation of Volume XV of the Transactions of the P. N. Lebedev Physics Institute, U.S.S.R.) Consultants Bureau, New York, 1962. 45 pp. $15.00.

Experimental spectroscopy in the optical region is considered to be a highly developed subject that has had most of its possibilities thoroughly explored; but, in fact, some branches of spectroscopy have barely been touched. The paper under review deals with the observations of widths and shifts of atomic lines in spark and arc discharges. While it is possible to determine the wavelengths of these lines with an accuracy of one part in several million, their widths can only be determined with an accuracy (by the author's own account) of about 20%! On the other hand, information about line-widths is of very great interest in the study of interatomic and intermolecular forces; the possibilities in this field are vast.

Experimental results are presented on the widths and shifts of about 50 lines (He, Ne, A, Fe) in the region of 4000 Å emitted from the plasma of a spark discharge. Five lines of Ca I are studied in the plasma of an arc. The experimental details are described fully. The spectra are recorded photographically, and line profiles are measured with a microphotometer. Shifts are measured by comparing the lines of the arc and spark with corresponding lines of a hollow-cathode discharge tube. Collisional line-widths are difficult to measure accurately because the observed line profile has to be corrected for finite instrumental slit-width, Doppler width, and scattered light and depends upon the accuracy of calibration of the photographic plate. Line shifts, on the other hand, although usually rather small, can be measured directly without making any instrumental corrections to the observations, provided the lines are symmetrical. With asymmetrical lines, the determination of both width and shift is neither easy nor reliable. Most of the lines observed in this work are symmetrical, although some asymmetrical lines are studied.

The observations are interpreted by means of a dynamical collision theory of Weiskopf-Lindholm type, after a criterion for its applicability is applied. The observations on the spark lines are considered easier to deal with because the perturbers of the emitting atoms all are taken to be charged particles and only one type of interaction (quadratic Stark effect) has to be included. An estimate is made of the electron density in the spark. In the arc, the perturbers are considered to be both charged (20%) and neutral (80%) particles, the latter exerting Van der Waals forces only.

Emphasis is given to comparison of the predicted and observed values of the ratio of width and shift of a line. Qualitative agreement between theory and observation is achieved in some cases, but the situation is far from satisfactory. (That the collisional width of a spectral line is proportional to the density of perturbers surrounding the emitting or absorbing atoms, a fact first stated by Lorentz over half a century ago, remains the only really reliable result of line-shape theory!) The author expresses the opinion that the theory would be improved by inclusion of inelastic collision cross sections. In addition, two other elaborations may be suggested: inclusion of elastic head-on collisions (Schuller and Vodar) and taking into account spatial degeneracy of the atomic states (Anderson).

The work constitutes the author's dissertation for the degree of Candidate of Physical-Mathematical Science. It draws the attention of Western readers to activity in this field in the U.S.S.R., although translations of Sobelman's reviews have been widely read. In an appendix, a list is given of the papers published (1932–60) by workers in the Spectroscopy Laboratory of the P. N. Lebedev Physics Institute of the Academy of Sciences of the U.S.S.R.

The English translation is excellent.

J. H. Jaffe

On Spectral Excitation in a Spark Discharge. By N. K. Sukhodrev. (Part 3 of an authorized translation of Volume XV of the Transactions of the P. N. Lebedev Physics Institute, U.S.S.R.) Consultants Bureau, New York, 1962. 45 pp. $12.50.

This review covers recent work done at the Lebedev Institute in four main areas: (1) Elementary Processes of Excitation and Ionization of Atoms in a Spark Discharge, (2) Measurement of Spark Temperatures, (3) Discussion of Available Temperature Data, and (4) Electrode Processes in a Spark Discharge. The discussion is well organized and quantitative, covering many points of direct interest to spectrochemists and others concerned with the fundamental properties of the spark. Section 1 proves, for instance, that the main role in the elimination of excited atoms and ions in the plasma of a spark is played by collisions of the second kind with electrons, and also shows that the principal process in ion-electron recombination is a three-body collision (ion + 2 electrons). Succinct derivations are also given in regard to the time of establishment of electron-temperature and ionization equilibria, and the establishment of an "excitation temperature" in the spark. Sections 2 and 3 describe the Institute's apparatus for making time-resolved measurements of the temperature of the spark channel, and discuss data obtained with it. Most measurements were made by the Ornstein method, using lines of N I, N II, and N III. These sections also present fundamental information on the effect of temperature on the populations of various species. Temperatures of $\geq$30,000°K were observed in spark channels, although it must be remembered that much of the light emitted by metallic sparks (and used in analytical work) comes from the cooler outer portions of the discharge. Electrical circuit parameters have relatively little effect on channel temperature, although they may affect line intensities quite strongly. Section 4 deals in some detail with energy balance and kinetics considerations in the volatilization of metal from electrodes. It is shown that metal is ejected from electrodes at $\sim 10^5$ cm/sec. This metal is at a relatively low temperature as it leaves the electrode, and becomes luminous only by passage through the channel region. Observations of sparks made with the microscope, image converter, and rotating mirror indicate that several cathode spots exist simultaneously, the current density being $\sim 5 \times 10^6$ A/cm^2.

The translation is accurate and idiomatic; the choice of equivalent English technical terms is faithful, with only a very few exceptions (e.g., "loop" instead of "circuit"). The survey is very much worth reading, and would make an admirable nucleus for an advanced textbook on spectroscopic light sources.

Cyrus Feldman

Editor's Note: We were grieved to note, as another OSA publication, that a supplemental listing of Russian physics journals translated in the U.S., included with this volume by the publisher, fails to mention OSA's translation journal *Optics and Spectroscopy*.

Books *continued on page 740*

A Vacuum Ultraviolet Photoionization Detector

A. K. Stober, R. Scolnik, and J. P. Hennes

A small ceramic ion chamber has been developed for a rocket astronomy program in the vacuum ultraviolet. The chamber consists of a small metal-plated ceramic shell incorporating a window of LiF, CaF_2, or BaF_2 and containing a filling gas of nitric oxide, acetone, carbon disulfide, or others. Typical quantum yields range from 8–10% for acetone with CaF_2 window to 50–60% for carbon disulfide with LiF window. Details of the chamber construction are given, and some recent applications of the detector are described.

Introduction

As part of a continuing program of observations of astrophysical and geophysical quantities in the vacuum ultraviolet wavelength region a small ceramic photoionization chamber has been developed at the Goddard Space Flight Center. These ion chambers, intended primarily for photodetection in the 1500 Å to 1050 Å wavelength region, have proved useful in a space science program which has included rocket- and satellite-borne experiments designed to measure both solar and stellar fluxes, as well as upper atmospheric emissions.

Ion chambers and photon counters were first used in a series of rocket experiments carried on at the Naval Research Laboratory in the 1950's. The literature contains several accounts of these vacuum ultraviolet detectors,[1,2] and the experimental results obtained from their use.[2–5] When the space science program at Goddard Space Flight Center was established in 1959 the experience gained from use of these earlier photoionization detectors was employed to design the present chamber. A brief description of the NASA ion chamber appears in a review of current ultraviolet photodetector developments by Dunkelman.[6]

Design Details

Gas ionization photodetectors have the useful properties of high spectral selectivity and relatively high quantum efficiencies. They can also be made very rugged and very compact. If meticulous attention is given to a number of fabrication details,[7] the NASA ionization chamber has the capability of having a long "shelf life", and of having the low noise and the stability needed for measuring very small incident photon fluxes (100–1000 photons/sec). Specifically, electrical leakage between electrodes must be minimized—a 10^{15} Ω path is easily achieved; photoelectric emission from the chamber walls must be reduced; recontamination of the filling gas after purification must be avoided; and window and connector seals must hold a high vacuum—better than 1×10^{-6} torr. The NASA ion chamber, Figs. 1 and 2, was designed to satisfy these requirements.

The chamber consists of a ceramic shell, gold-plated on the inside, fitted with a highly polished central collecting wire electrode and incorporating a window of suitable transmission properties. The shell, which has an external lip to provide a surface for making an O-ring seal into either the exit port of a vacuum monochromator or the skin of a rocket or satellite package, is usually fitted with an 11-mm diam crystal window and has an inside diameter of 1.9 cm and an inside length of 2.3 cm.*

The ceramic shell† itself is of a high density alumina and is plated on the inside with several layers of metallic coatings, finishing with a gold plate on the surface, to form one of the electrodes. Brazed into the unplated rear face of the tube are a kovar central pin electrode, a guard-ring and connector and a 10-cm long, copper, gas-filling tube which also provides the

The authors are with the Goddard Space Flight Center, National Aeronautics and Space Administration, Greenbelt, Maryland.

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Presented at the Los Angeles meeting of the Optical Society of America, October 1961.

* Ceramic ion chambers of this design are now commercially available from the Geophysics Corporation of America, Bedford, Mass., and Melpar, Inc., Falls Church, Va.

† Manufactured by the Coors Porcelain Company, Golden, Colorado.

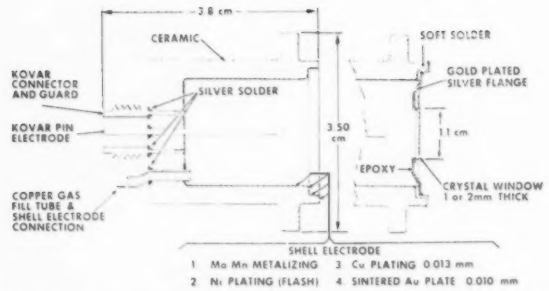

Fig. 1. Cross section of the NASA ion chamber. The inside diameter of the chamber is 1.9 cm and length 2.3 cm. Window materials are generally of LiF, CaF_2, or BaF_2 crystals.

electrical connection to the metal-plated shell electrode.

The ion chamber window, usually consisting of 1- or 2-mm thick cleaved crystals of LiF, CaF_2, or BaF_2, is fastened to a thin gold-plated silver flange by an epoxy layer. The flange, whose 9.5-mm diam defines the aperture of the chamber, is soft-soldered onto the metalized ceramic shell prior to forming the window seal. The sealed tube is baked at 100°C for several hours. The assembled chamber is evacuated through the copper, gas fill tube, while being heated to 100°C, until a pressure of 1×10^{-6} torr or less is reached. The filling gas, which has previously been distilled from a supply of commercial "pure" gas, is admitted through the tube and the chamber sealed by pinching the copper tube closed and dipping the tube end in solder.

The choice of the ceramic chamber ensures the ruggedness and low-electrical leakage desired and provides a surface which is resistant to contamination. The gold plating on the chamber walls provides both a conducting surface with low-photoelectric emission and a high work function,[8] and one that will not react with any of the chemicals used as filling gases. In addition, by keeping the entrance window small and leaving the rear wall of unplated ceramic (except for the center pin, guard ring, and gas-filling tube), the amount of photoemissive surface exposed to the incident flux is

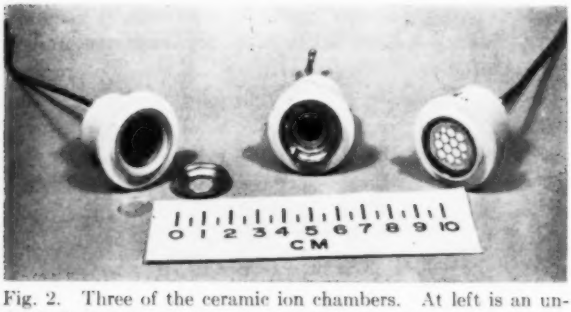

Fig. 2. Three of the ceramic ion chambers. At left is an unfinished chamber with window and flange. In the center is a completed tube. At right is a tube with a thin aluminum window for x-ray use.

kept to a minimum. The epoxy, soft-solder window seal has proved very tight and, since high-temperature baking is not required, quite stable over long periods of time. The general success of these design features can be demonstrated by the almost zero rejection rate which has been achieved in assembly of chambers and by the existence in our laboratory of ion chambers assembled almost two years ago which still maintain their quantum yields. A single exception appears to be a diethyl sulfide ion chamber with barium fluoride window. These chambers have a spectral bandpass from 1350 to 1480 Å and an efficiency approaching 20%, but the few detectors made have had a shelf life of little more than one month. The investigation of gas purification and anti-recontamination is in the early stages of attempting to increase the "shelf life" of this detector.

The short wavelength limit of the spectral response of these chambers is usually determined by the transmission cutoff of the window materials. In addition

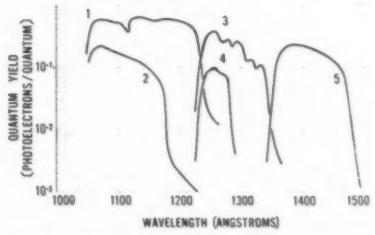

Fig. 3. Typical ion chamber spectral response curves for several gas and window combinations. Smoothed curves are shown although a certain amount of fine structure is obscured in so doing: 1. Carbon disulfide with LiF window; 2. ethylene oxide with LiF window; 3. nitric oxide with CaF_2 window; 4. acetone with CaF_2 window; 5. Diethyl sulfide with BaF_2 window.

to the LiF, CaF_2, and BaF_2 crystals mentioned above, windows of NaF or sapphire may also prove useful. The transmittance curves of these materials are included in a paper by Dunkelman *et al.*[9] Also used with these ceramic ion chambers have been windows of thin (0.03–0.2 mm) foils of aluminum and beryllium. When used with a filling gas such as xenon these ion chambers become useful x-ray detectors in the 2–8 Å region. Window materials and filling gases for use in either the vacuum ultraviolet or x-ray region have been tabulated by Friedman.[2]

Pictured in Fig. 2 are some of the chambers discussed herein. At the left is an unfinished shell with a window flange and LiF window. In the center is a completed ion chamber and at the right one of the x-ray chambers mentioned above.

Detector Characteristics

In normal use the ceramic ion chamber is operated with the guard ring at ground potential and the shell

Table I. Typical NASA Ion Chamber Characteristics

Gas filling	Chemical formula	Gas pressure (torr)	Window material	Window thickness (mm)	Spectral response region (Å)	Typical quantum yields[a] (photoelectrons/photon)
Diethyl sulfide	$(C_2H_5)_2S$	5	BaF_2	1	1350–1480	0.10–0.20
Nitric oxide	NO	20	CaF_2	1	1230–1350	0.20–0.30
Nitric oxide	NO	20	LiF	1	1050–1350	0.30–0.40
Acetone	CH_3COCH_3	4.5	CaF_2	1	1230–1290	0.08–0.10
Carbon disulfide	CS_2	15	LiF	1	1050–1240	0.50–0.60
Ethylene oxide	$(CH_2)_2O$	4.5	LiF	1	1050–1180	0.10–0.20
Xenon	Xe	775	Be	0.13	2–8	Not measured

[a] Based on an absolute photoionization yield of 0.81 ion pairs/photon for NO at Lyman-alpha.

electrode at −45 to −90 V, depending on the gas filling. When it is necessary to suppress photoelectric emission from the walls completely, the shell electrode is operated at a positive potential. In many applications, however, the available flux is so exceedingly small that it is necessary to operate these tubes as gas-gain detectors. If the collecting voltage is raised past the low-voltage plateau region the output current increases in an exponential fashion. Gains of 1000 are generally attainable with voltages of 600 to 800 V. The shell electrode carries the negative high voltage in this case.

A variety of filling gases have been used with these tubes. The choice of the gases is determined by the spectral region of experimental interest and, of course, it fixes the long wavelength cutoff. The stability of the gas when incorporated in an ion chamber determines whether any specific gas can make a useful detector. Figure 3 shows the spectral response of five of the gas-window combinations which have been used in ion chambers in rocket-borne experiments by Goddard Space Flight Center. The curves represent smoothed values of quantum-yield as measured on a McPherson 1-m vacuum monochromator operating with a resolution of 3–4 Å. Some of the fine structure of nitric oxide is shown in curve 3 but most of the details do not appear.[10–12] Of particular interest are the relatively narrow response bands and the fairly high, quantum-yields. The measured quantum-yield of any given chamber is a combination of the actual photoionization yield of the gas, the transmittance of the window, the absorption efficiency, and ion collection efficiency of the chamber.

Table I lists some of the gas and window combinations used in our space science program and gives some of the most pertinent features of these ion chambers.

Calibration

The shape of the spectral response curves are determined by a comparison of the ion chamber response to a hydrogen arc lamp with the response of a sodium-salicylated detector to the same lamp. The fluorescence yield of sodium salicylate is assumed to be fairly constant over this wavelength region from 1500 Å to 1000 Å.[13] Measurements were made at the exit slit of the 1-m vacuum monochromator mentioned above. Absolute quantum-yield values were determined by a direct comparison of the signal from the ion chamber in question, when exposed to Lyman-alpha (1216 Å) radiation, with the signal from a reference "standard" ion chamber[7] exposed to the same beam. The reference ion chamber is a large volume, windowless, glass cylinder containing large, flat, plane-parallel collecting electrodes for both efficient absorption of the incident flux and efficient collection of the ion-pairs produced. The electrodes are rigidly mounted to avoid vibration pickup.

Calibration of the ion chamber quantum-yields are based on the absolute photoionization-yield of nitric oxide (NO) at the Lyman-alpha wavelength (1216 Å). From the work of Watanabe[14] this yield is taken to be 0.81 ion-pairs/photon. The flat sodium salicylate response is used to transfer the quantum-yield measurements from Lyman-alpha to other wavelengths when the efficiency of the gas being measured is required for wavelengths other than Lyman-alpha.

Applications

The NASA ceramic ion chambers were first used successfully in the spring of 1960 in a series of Aerobee-Hi rocket experiments designed to survey the northern night sky.[15] Ion chambers containing nitric oxide, acetone, or carbon disulfide were positioned at the foci of 10-cm diam collecting mirrors which scanned the sky as the rocket rolled and precessed. Because of the weak signals expected from stellar sources the ion chambers were operated with gas gains of about 200. The signals observed were on the order of 10^{-12} A with this system, indicating a flux of about 10^{-7} ergs/sec cm.^{2}

In August–November 1961 a similar survey of the southern hemisphere night sky was obtained from a series of Skylark rocket firings from Woomera, Australia.[16] A single rocket carried four ion chamber tele-

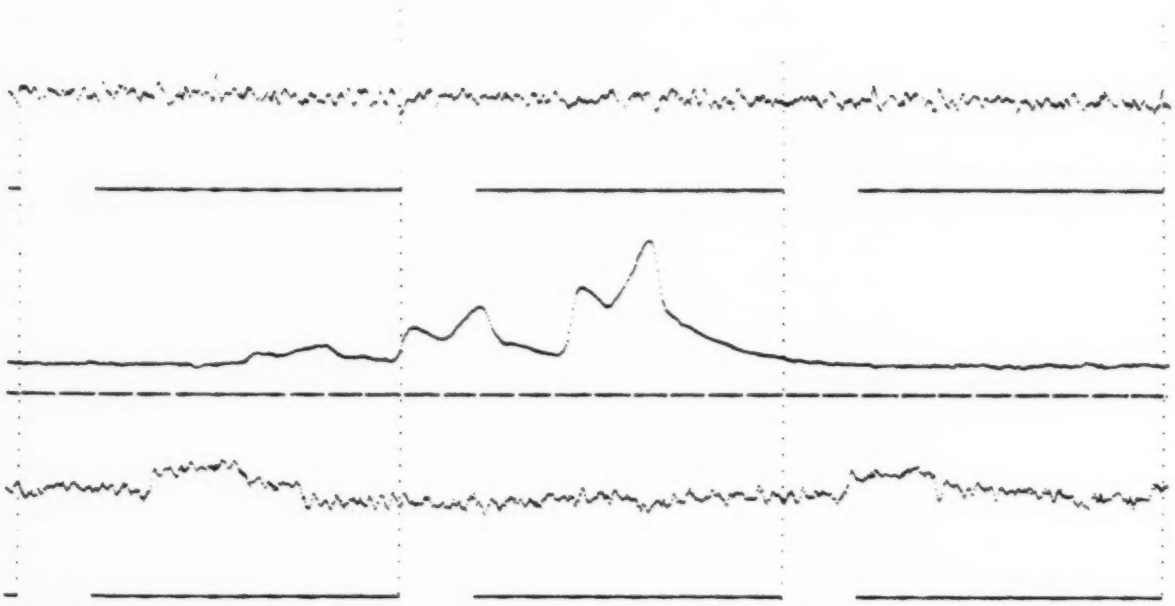

Fig. 4. Telemetry record showing a 3-sec portion of several detector signals: the top and bottom channels are signals from photomultiplier photometers; the middle channel is the signal from an ion chamber telescope. The difference in detector noise levels is evident. Three double-peaked ion chamber star signals are shown. The unsymmetrical shape of these star signals is caused by telescope geometry (see text).

scopes, each consisting of two chambers located alongside one another at the focus of a 15-cm diam mirror. Useful signals were obtained from about 60 stars with the ion chambers operating at gains of 300–500.

Figure 4 shows three seconds of a typical telemetry record from this flight. The top and bottom channels represent middle ultraviolet photomultiplier photometers. The middle channel gives the signal from an ion chamber telescope. The difference in noise level of the two types of detector is evident. The three double-peaked ion chamber signals represent the sweep of the ion chamber telescope across three stars as the rocket slowly turned. The asymmetry of the right and left parts of each double-peak is produced by the off-axis location of the ion chambers, which causes the effective mirror aperture to change as the star moves across the field of view. The double-peak itself is a function of the position of the highly convergent beam in the ion chamber cavity. When the ion chamber is operated in a collimated beam the angular response to a point source is more or less flat-topped. When the chamber is operated in a highly focused beam the central region of the telescope angular response signal may be depressed by as much as 75%. The choice of focus conditions presents different problems which the experimenter must resolve for himself.

More recently these ion chambers have been used in the Orbiting Solar Observatory, launched in March 1962, to observe the sun in two wavelength regions. One ion chamber, of nitric oxide with a LiF window, periodically observed the solar Lyman-alpha emission from behind an aperture of about 0.4-mm diam. Two others, operated in parallel with 0.13-mm thick beryllium windows and xenon gas, continuously measured the sun's x-ray emission in the 2 Å to 8 Å region. Other current uses include a rocket-borne ion chamber for measurement of the Lyman-alpha radiation emitted from the top of the earth's atmosphere and a Lyman-alpha detector in an ionosphere probe to measure the rate of photoionization in the D region.

Perhaps the most important use for these detectors is as stable vacuum ultraviolet photodetectors for laboratory purposes. By combining the simple physical principles of gas ionization with a vacuum-tight and stable chamber a very useful reference standard for laboratory spectroscopy can be obtained.

The basic ion chamber design was suggested by J. E. Kupperian, Jr., the use of a ceramic shell was suggested by E. V. Serra, the choice of an epoxy was suggested by W. A. Gallo, Jr., and E. V. Serra assisted in the development of the epoxy window sealing technique.

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Meeting Reports *continued from page 726*

line shapes in pressure-induced absorption. Margenau and Roger Herman, with the precise, well-ordered technique we so thoroughly appreciate, gave a comprehensive survey of the theory of line shapes, of the why's and wherefore's of impact and statistical approaches; and was followed by R. G. Breene, Jr., who devoted himself to induced intensities. The fourth session showed the impact of the space age. It began with Fastie *Johns Hopkins*, whose beautifully designed spectrometers are obtainmg the best airglow measurements by rocket spectral photometry. He was followed by Singer (*Maryland* and the National Weather Satellite Center) who spoke on atmospheric sounding by satellite spectroscopy, a subject still largely in the planning stage. Goldberg *Harvard* gave a remarkably detailed review of solar spectroscopy in his allotted time and was followed by Kaplan *JPL* who reviewed the Mariner II Venus Shot, together with Barrett *MIT*. As is now well known, the microwave equipment behaved rather better than the infrared radiometers, but one can have only admiration for the care in both experimental design and engineering of the whole project. The fifth and last session was devoted to planetary spectroscopy, with Herbig *Lick* starting the morning off with interstellar spectroscopy, followed by Sandage who spoke on the cosmological problem. His review, coming as it does from the Mt. Wilson-Palomar group which has in the last few years added so much to our knowledge as well as to the puzzle of the age of the universe, was enticing and most appropriate. Chamberlain *Kitt Peak* gave a clear status report on where we stand on our knowledge of the dayglow spectra of the planets, and the meeting was closed out by Sinton *Lowell* who spoke on the recent spectra of Mars and Venus. The water-vapor problem, while not yet solved quantitatively, as the title of this conference indicated it should be, is steadily being more and more closely bracketed.

On the social side, arrangements left very little to be desired. The weather was chamber of commerce stuff, with clear sunshine and no smog. Since the meeting was held during the spring recess, the campus was open for visiting friends and colleagues at leisure. The banquet was well attended, and those of us who had the opportunity to hear William Pickering, director of JPL, speak after dinner, have a first-hand account of the spirit and *modus vivendi* of part of the Space Age environment.

To sum up scientifically, this reporter thinks that one could say that a rather good deal of orderly progress is being made in the matter of getting better and more meaningful f numbers for a number of species; our success seems to be somewhat limited, however, for some cases of extreme interest to the tracking and re-entry problems. Moreover, it is evident that rocket spectroscopy is a lively field from x rays to the infrared, and astrophysics in general is a marvelous hunting ground for spectroscopists. Lastly, from the youthfulness of many of the attendees, the diversity of their interests, and the general enthusiasm, it would seem that quantitative spectroscopy plans a lively role in our scientific goings-on. It is to be hoped that Penner and Caltech will see fit to sponsor another conference in 1966.

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1921	V	4	July–Aug.
1921	V	5	Sept.–Oct.
1921	V	6	Nov.–Dec.

Books *continued from page 734*

The Radioluminescence Yield of Organic Scintillators. By Z. A. Chizhikova. (Part 4 of an authorized translation of Volume XV of the Transactions of the P. N. Lebedev Physics Institute, U.S.S.R.) Consultants Bureau, New York, 1962. 50 pp. $12.50.

This work describes several experimental studies related to the efficiency of the scintillation process in organic materials which have been undertaken by the author under the direction of M. D. Galanin during the past few years. These include (1) the determination of the absolute photoluminescence quantum yields of several organic crystals; (2) a measurement of the absolute scintillation efficiency (2.1%) of a trans-stilbene crystal excited by γ-rays; (3) a comparison of the scintillation and photofluorescent efficiencies of several organic crystals and the evaluation of the mean-excitation efficiency (4.1%) of the scintillations; (4) a study of the intensities of the radioluminescence and Cerenkov radiation from solutions of fluorescent solutes in "poor" (non-energy-transferring) solutes, from which a mean value of 3.9% is obtained for the excitation efficiency of the scintillations from "isolated" molecules; and (5) an investigation of the quenching of the luminescence excited by α particles (the determination of the α/β ratio) in organic crystals, plastic solutions, and liquid solutions, and of the influence of the concentrations of solute (*p*-terphenyl) and impurity (carbon tetrachloride) on the α/β ratio in xylene solutions.

Although the main results have been previously published in *Optics and Spectroscopy* and *Soviet Physics—JETP*, their integration and discussion in this monograph enables them to be seen in clearer perspective as a significant contribution to our knowledge of the organic scintillation process.

J. B. Birks

Report on Available Standard Samples and Related Materials for Spectrochemical Analysis 1960. Compiled by R. E. Michaelis. Special Technical Publication 58-D, American Society for Testing Materials, Philadelphia, 1961. 122 pp. $3.75.

This small volume represents the fourth and expanded revision of collected information dealing with most of the known available standard samples for spectrochemical analysis.

Calibrated standard samples for metals and their alloys covering aluminum, iron, copper, nickel, die-casting materials, and others as supplied by fifteen suppliers are described regarding size, composition, and intended used. Some of the NBS standards cited are specifically intended for x-ray fluorescence analysis rather than optical emission work. Other listed standards include ores, ceramic materials, diesel-oil contaminants, metallo-organic compounds, and ground materials for tree leaf analysis. Several types of reference materials for semiquantitative analysis are described by their composition, application, and where they may be obtained. Another section describes the available high-purity inorganic materials such as metals, sponges, foil, compounds, and solutions. In most cases, the cited purity ranges from 99.5 to 99.9995%. More than 850 entries available from over 60 suppliers are noted.

This report should be on the book shelf in all spectrochemical laboratories, and will also serve as a handy and valuable reference to workers in solid state, semiconductor, biological, and other fields requiring materials of the highest purity.

Edwin S. Hodge

Advances in Spectroscopy. Edited by H. W. Thompson. Vol. II. Interscience Publishers, New York and London, 1961. 483 pp. $13.00.

The second volume of *Advances in Spectroscopy* is reminiscent of one of those memorable feasts that are held from time to time in certain halls of learning. The chief steward, Dr. Thompson, has invited 10 internationally renowned chefs for the occasion, each to prepare his own *spécialité*. The result is a gourmet's paradise in which all tastes are catered to, from the x-ray to the radio-frequency region (except for the few that are peculiarly sensitive to microwaves). All ranges of molecular appetite are satisfied, from those who enjoy their atoms individually to those who prefer the more exotic molecular aggregates or even micro-organisms.

An interesting antipasto is provided by A. Walsh (Melbourne), entitled "The Application of Atomic Absorption Spectra to Chemical Analysis"; it is followed by a *préparation flambée*, "The Spectra of Flames" by A. G. Gaydon (London). For contrast, the next two courses deal with "X-ray Spectroscopy" by H. Friedmann (Washington) and "Nuclear Magnetic Resonance" by R. E. Richards (Oxford). The former offering is commendably garnished with many fine diagrams; the latter work provides an excellent and substantial supplement to the *chef d'oeuvre* of Pople, Bernstein, and Schneider. An authoritative treatment of the "Infra-red Spectra of Crystals" is next served jointly by W. Veddar and D. F. Hornig (Princeton) and is followed by an interesting preparation on the "Refraction of Gases in the Infrared" by J. H. Jaffe (Rehovoth). Two *spécialités* with a biochemical flavor are the "Infra-Red Spectra of Micro-Organisms" by K. P. Norris (Porton, England) and "The Ultra-Violet Absorption Spectra of Proteins and Related Compounds" by G. H. Beaven (London). A memorable *crêpe suzette* is provided by H. C. Longuet-Higgins (Cambridge), entitled "Some Recent Developments in the Theory of Molecular Energy Levels", in which the intricate motions of electronically degenerate species are treated with characteristic artistry and finesse.

To consume such a variety of excellent courses is liable to produce spectroscopic indigestion in all but the hardiest connoisseurs, and many gastronomes will be content with merely a judicious selection. It is unfortunate that some of the courses were slightly impaired by the undue delay between the preparation and the serving. Nevertheless, the *Chateau Thompson* can be heartily recommended; the *décor* is very pleasing, and *l'addition* is quite reasonable.

D. A. Ramsay

Molecular Spectroscopy. International Union of Pure and Applied Chemistry, Physical Chemistry Section, in conjunction with Royal Netherlands Chemical Society and Netherlands Physical Society. Butterworths, London, 1962. 189 pp. 40 shillings.

The book gives the full text of the 2 general and 15 introductory lectures presented at the Fifth European Congress on Molecular Spectroscopy held in Amsterdam in 1961, as reprinted from *Pure and Applied Chemistry* **4,** No. 1 (1962).

In the general lecture on vibrational-rotational spectra presented by E. B. Wilson, Jr., certain selected topics referring to unpublished work from the group at Harvard are discussed in order to illustrate some present-day capabilities, particularly with respect to the determination of molecular structure, elucidation of rotational isomerism, measurement of barriers to internal rotation, and the study of nonbonded forces. Dr. Wilson's conclusions referring to the accuracy of the determination of the structural parameters of larger molecules that can be achieved by microwave spectroscopic methods are of the most general

continued on page 764

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Infrared Dispersion of Some Oxide Glasses

I. H. Malitson, G. W. Cleek, O. N. Stavroudis, and L. E. Sutton

The refractive indices of silicate, germanate, calcium aluminate, and tellurite glasses have been determined in the wavelength range from about 0.4 μ to 5.3 μ. The experimental data for the silicate and germanate glasses were fitted to a Sellmeier dispersion equation of the form $n^2 = 1 + \Sigma A_i\lambda^2/(\lambda^2 - \lambda_i^2)$. Dispersive curves were plotted which indicate the expected dispersion, contribution to chromatic aberration, and resolution of the glasses as a function of wavelength.

Few refractive-index data are available in the literature for oxide glasses at wavelengths beyond about 2.5 μ. Stephens and Rodney[1] have reported the refractive indices and the dispersion equations for five optical glasses to 2.32 μ. Similar data for fused-quartz glass to 3.5 μ have been determined by Rodney and Spindler.[2] Cleek *et al.*[3] reported the refractive indices and transmittances of several optical glasses to 4.25 μ.

Perhaps one of the reasons why few dispersion data are available at the longer wavelengths is that most commercially made glasses have rather strong absorption bands in the vicinity of 2.75 μ that are attributed to (OH)-radicals in the glass structure.[4] As a result, not enough energy gets through a prismatic sample for accurate refractive-index measurements. The data reported in this paper were obtained on experimental glasses that had considerably better transmittance in the infrared than most commercially available glasses.

Vincent-Geisse and Lecomte[5] have reported on various methods of making refractive-index determinations in the infrared. These methods depend on the regions of relative transparency of a given material. In regions of good transparency, prismatic methods were used; for liquids and in regions of weak absorption, a method using interference spectra was employed; in regions of strong absorption, a reflection technique at a near-normal angle of incidence was used; and, finally, in certain cases, Christiansen filters proved useful. By a combination of these methods, a dispersion curve for a Parra-Mantois glass, D2828, (n_D = 1.728) was obtained for the wavelength range from about 0.5 to 14 μ. Thus, it is shown that techniques are available to obtain data at the longer wavelengths. This is of interest from the point of view of dispersion theory.

The authors are with the National Bureau of Standards.
Received 24 September 1962.

Oxide glasses are now available that are useful to about 6 μ, and data on these glasses are of interest to the optical designer. Reports on the optical properties of materials generally contain little information on glasses.[6,7] Actually, glasses have certain advantages over other materials for use in infrared optical devices. The optical properties of homogeneous glass are constant in all directions in the material, and orientation is not a problem in grinding and polishing. The refractive indices of glasses can be varied from melt to melt by appropriate composition changes, and a fairly wide range can be obtained. The temperature coefficient of transmissivity for glasses is usually low, and little loss in transmission is found at 400°C or higher.

Types of Glasses

The purpose of this paper is to report on the dispersion curves of four different types of oxide glasses and to present the results obtained when the measured values of refractive index were fitted to a Sellmeier dispersion equation. The four types of glasses that have been investigated were made at the National Bureau of Standards and are (1) barium titanium silicate glass, (2) barium titanium germanate glass, (3) calcium aluminate glass, and (4) tellurite glass. The oxide compositions of the glasses as determined from batch are shown in Table I. The useful limits of transmittance of the various glasses studied are indicated in Figs. 1–7, which show transmittance and absorption coefficient vs. wavelength.

Measurement and Calculation of Refractive Index and Dispersion

The refractive-index data given in Table II and plotted in Fig. 8 for the barium titanium silicate glasses, the barium titanium germanate glass, and the calcium aluminate glass were measured on a precision spectro-

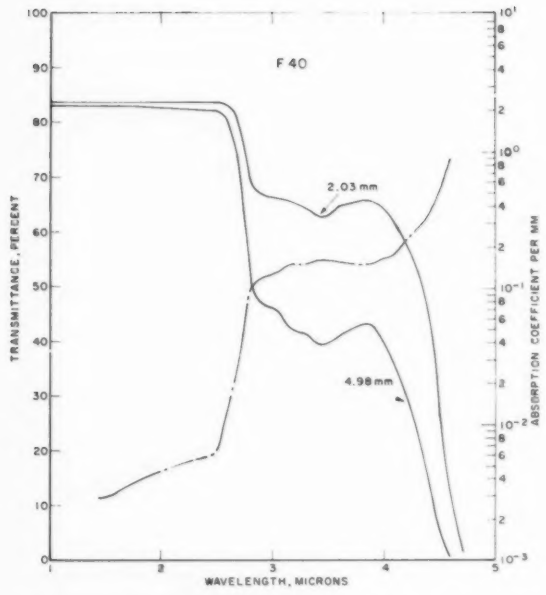

Fig. 1. Transmittance of two thicknesses and calculated absorption coefficient as a function of wavelength for glass F40.

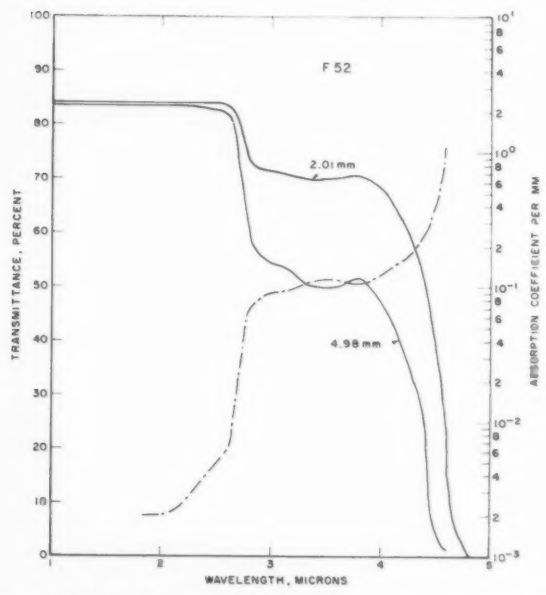

Fig. 2. Transmittance of two thicknesses and calculated absorption coefficient as a function of wavelength for glass F52.

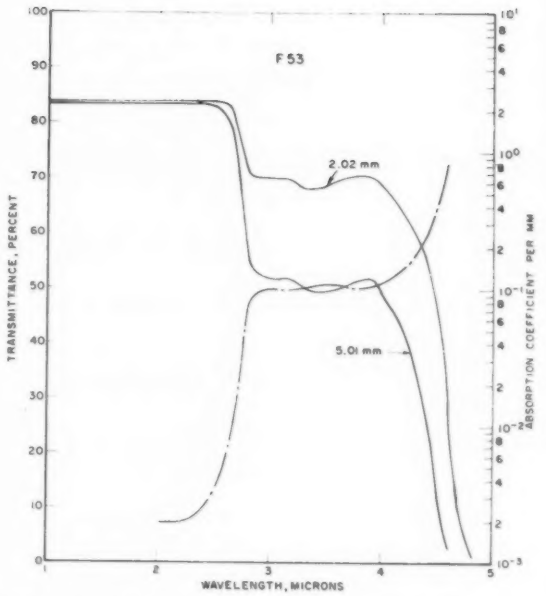

Fig. 3. Transmittance of two thicknesses and calculated absorption coefficient as a function of wavelength for glass F53.

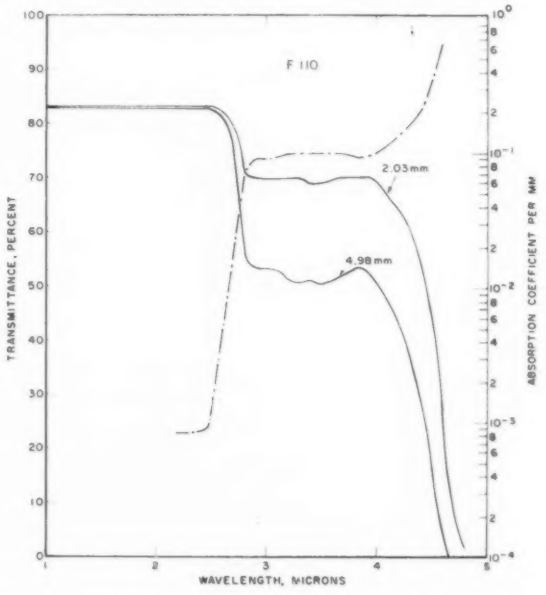

Fig. 4. Transmittance of two thicknesses and calculated absorption coefficient as a function of wavelength for glass F110.

meter by the minimum-deviation method. The indices were determined for some 50 calibrated wavelengths of various emission sources and absorption bands over the wavelength range from 0.4 μ to 5.4 μ. The room temperature was regulated and maintained near 24°C. A description of the instrument and the procedure used in making the measurements are contained in a previous publication.[8] The tellurite glass was measured by the Eastman Kodak Company under BuOrd sponsorship by a method described by McAlister *et al.*[9] The data are included here to show that the dispersion curve for this glass is very similar to those of other oxide glasses.

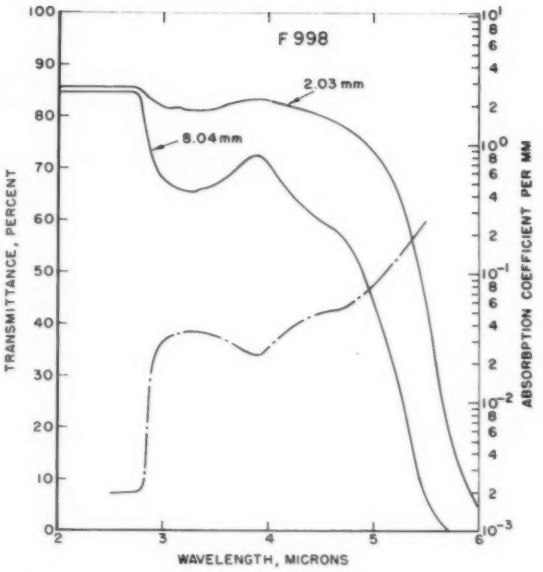

Fig. 5. Transmittance of two thicknesses and calculated absorption coefficient as a function of wavelength for glass F998.

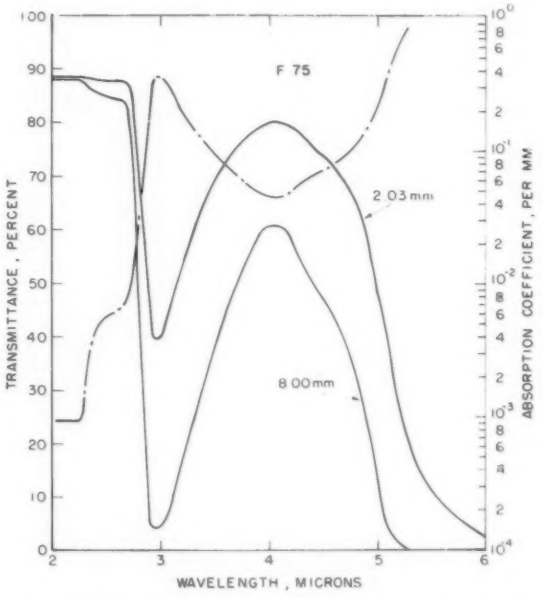

Fig. 6. Transmittance of two thicknesses and calculated absorption coefficient as a function of wavelength for glass F75.

The index-of-refraction measurements thus obtained are at discrete values of wavelength for which calibrated emission sources or absorption bands are available. The designer of optical instruments needs to know the refractive and dispersive properties of his optical material over a range of wavelengths, including many specific wavelengths intermediate to those at which the measurements were made. Clearly, a very accurate means of interpolation is called for.

At the National Bureau of Standards, we have been successful in fitting up to 50 index-of-refraction determinations very accurately to a three-term Sellmeier equation. In this work, the index measurements cover the wavelength range from 0.26 μ to about 10 μ. The Sellmeier equation,

$$n^2 = 1 + \Sigma A_j\lambda^2/(\lambda^2 - \lambda_j^2),$$

is an idealized mathematical model representing the dependence of the index of refraction n at a wavelength λ on the wavelengths λ_j and magnitudes A_j of the absorption maxima. It is valid in a wavelength region bounded away from the λ_j. Optical materials exhibit absorption spectra much more complex than can be represented by three absorption maxima. Therefore, it is improper to identify too strictly the parameters of a three-term Sellmeier equation, as obtained by a least-squares fit, to refractive-index data, with the actual locations and magnitudes of the absorption maxima of the substance measured. Thus, in making such a least-squares fit, one must be certain that, over the wavelength range in which the data lie, there are no absorption maxima or that, if any are present, their magnitudes are so small that the associated Sellmeier terms can be neglected.

In the dozen or more optical materials analyzed in this manner, no difficulties have resulted. Indeed, a study of the residuals of fits of refractive index by the Sellmeier formula indicates that the parameters are determined with a precision consistent with the accuracy of the data. A detailed account of the method of computation may be found in the literature.[10,11]

Recently a number of other approaches to the problem of interpolating refractive-index measurements have appeared. Vagner-Dewulf *et al.*[12] use a two-term Ketteler-Helmholtz formula

$$n^2 = n_0^2 + \frac{A}{\lambda^2 - \lambda_1^2} - \frac{B}{\lambda_2^2 - \lambda^2},$$

where λ_1 and λ_2 are determined experimentally, and n_0, A, and B are determined by fitting to refractive-index measurements. Herzberger[13] uses

$$n = a + i_0\lambda^2 + \frac{c}{\lambda^2 - \lambda_0^2} + \frac{d}{(\lambda^2 - \lambda_0^2)^2},$$

in which $\lambda_0 = 0.168$ μ for all glasses, the remaining parameters being determined by a least-squares fit to refractive-index values. The results are suprisingly good, at least over the visible spectrum.

The values of index of refraction for each glass for which sufficient data were available were fitted to the Sellmeier equation in the manner described above. An average residual of about 5×10^{-5} indicates that intermediate values of index may be interpolated to four decimal places. The parameters so determined are given in Table III.

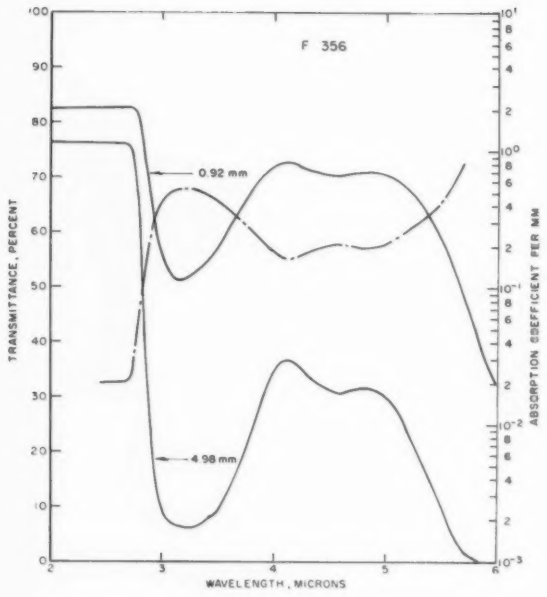

Fig. 7. Transmittance of two thicknesses and calculated absorption coefficient as a function of wavelength for glass F356.

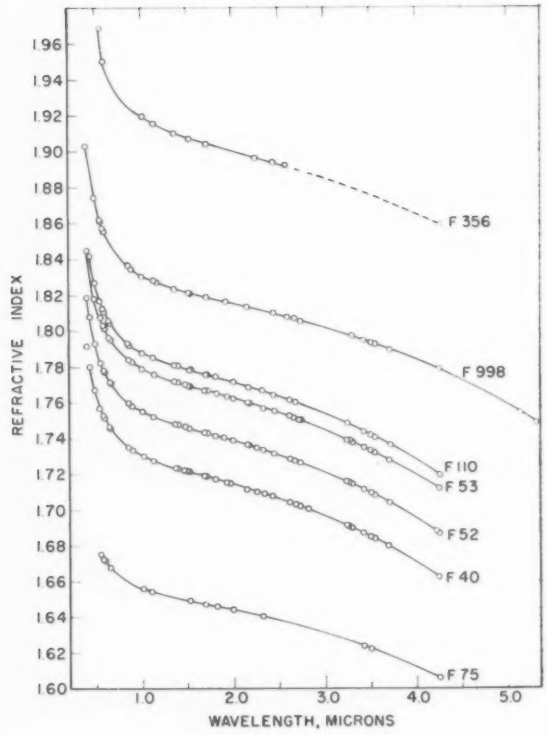

Fig. 8. Refractive index as a function of wavelength for seven experimental oxide glasses.

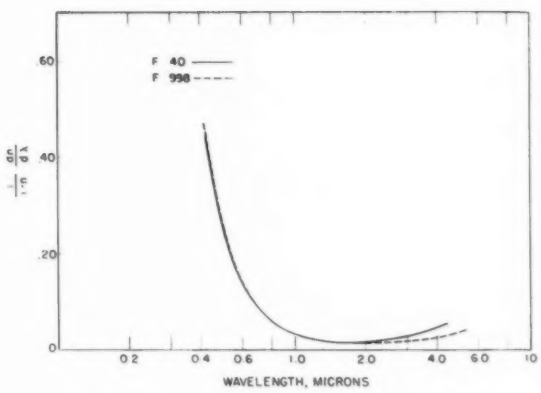

Fig. 9. Ratio of dispersion relative to deviation as a function of wavelength for glasses F40 and F998.

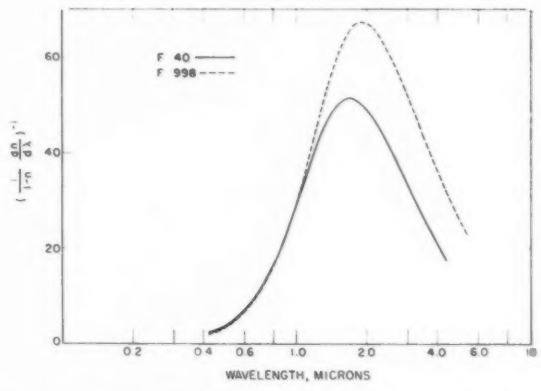

Fig. 10. Generalized ν-value $\{[(1/1 - n)\ (dn/d\lambda)]\}^{-1}$ as function of wavelength for glasses F40 and F998. As ν-value increases, the contribution to chromatic aberration decreases.

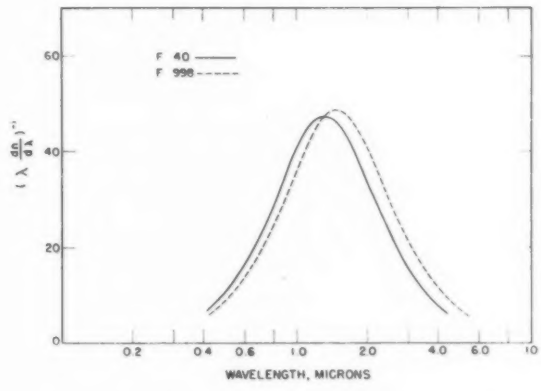

Fig. 11. The expected resolution as a function of wavelength for glasses F40 and F998. For best resolution, $(\lambda\, dn/d\lambda)^{-1}$ should be small.

The equations were used to compute values of refractive index n and dispersion $dn/d\lambda$ at small wavelength intervals from about 0.4 μ to about 5.5 μ. The derivative of the Sellmeier equation is used for $dn/d\lambda$ rather than values obtained by tabular differentiation based on finite difference methods. These values were then used to compute three quantities that indicate the dispersive properties of the glasses as functions of wavelength. The quantity $[1/(1 - n)](dn/d\lambda)$ is analogous to $1/\nu$, the *dispersive power* as defined for the visible region of the spectrum, and is the ratio of dispersion relative to deviation. Its reciprocal, $\{[1/(1 - n)](dn/d\lambda)\}^{-1}$, a generalized ν-value, is frequently used as a datum in calculating chromatic aberration. The quantity $(\lambda dn/d\lambda)^{-1}$, suggested by Conn and Avery,[14] can be considered as providing an estimate of the resolution to be expected from a prismatic material. These five calculations are done in less than a minute per glass on a high-speed computer.

It should be noted that these measures of dispersion involve only the index as a function of wavelength and are dependent only on the optical properties of the medium. They provide, therefore, information suitable for the estimation of the optical performance of a material.

Dispersive Properties of Some Infrared Glasses

The dispersive properties of a silicate glass (F40) and a germanate glass (F998) are plotted as a function of wavelength in Figs. 9, 10, and 11. Sufficient data were not obtained on the calcium aluminate glass and the tellurite glass to permit a detailed analysis of their dispersive properties.

Figure 9 is a plot of $[1/(1 - n)](dn/d\lambda)$, the dispersion relative to deviation. In general, considering the whole range of wavelengths, the dispersions of both glasses are very similar. The dispersion decreases with increasing wavelength, reaches minimum near 2.0 μ, then slowly increases as it approaches the long-wavelength limit. Specifically, the curves show that from about 0.9 μ and out toward longer wavelengths, the lower-index glass has the higher dispersion.

Figure 10 is a plot of the generalized ν-value $\{[1/(1 - n)](dn/d\lambda)\}^{-1}$. Here an increase in the ordinate values corresponds to a reduction in the contribution to the chromatic aberration of a lens using an element made of this glass. It can be seen that a minimum contribution occurs near 2.0 μ. The curves also show that for wavelengths longer than 1.0 μ, the contribution to chromatic aberration will be *less* for the higher-index glasses.

Figure 11 is a plot of the resolution as a function of wavelength. Here, the requirement is that $[\lambda(dn/d\lambda)]^{-1}$ be as small as possible. The curve shows that, in general, the optimum region for resolution is at wavelengths longer than about 2.5 μ in the infrared. Beyond 1.3 μ, the lower index glass should be expected to have the better resolution.

In general, the dispersive properties of glasses F52, F53, and F110 are almost identical to those of glass F40. The values of dispersion, chromatic aberration, and resolution fall between those of the plotted glasses and increase or decrease at corresponding regions of the spectrum as the refractive indices of the glasses increase. These glasses are anomalous in the sense that the one having the lower index has the greater dispersion in the infrared. Obviously, the constant ν is not a reliable criterion for estimating dispersion beyond the visible region of the spectrum.

Summary

The availability of high-speed electronic computers makes practicable the calculation of three quantities that indicate the expected dispersive characteristics of an optical medium. These measures of dispersion, which involve only the refractive index, suggest that for a specific material there are optimum regions of the spectrum for relative dispersion, low chromatic aberration, and resolution.

Table I. Compositions of Glasses in Mole Percent

Oxide	F40	F52	F53	F110	F998	F75	F356
SiO_2	50	50	50	50		5	
GeO_2					45		
BaO	30	26	22	20	18		
CaO						48.5	
TeO_2							84
Al_2O_3						41.5	16
TiO_2	20	20	20	20	10		
La_2O_3		4	8	10	7		
MgO						5	
ZnO					10		
Ba_2O_5					1		
TaF_2					4		
ZrO_2					5		

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Tables II, III, and References continued overleaf

Table II. Refractive Indices of Experimental Glasses

Melt no.		F40[a]	F52[a]	F53[a]	F110[a]	F998[b]	F75[c]	F356[d]
ν-values		34.6	34.3	34.3	34.4	32.9		
Wavelength (μ)	Source							
0.40465	Hg	1.79148	1.81859	1.84447		1.90302		
0.43583	Hg	1.78011	1.80682	1.83233	1.84181	1.88997		
0.48613	H	1.76721	1.79342	1.81851	1.82786	1.87470		
0.54607	Hg	1.75697	1.78274	1.80748	1.81677	1.86242	1.67524	1.9689
0.57696	Hg	1.75301	1.77864	1.80324	1.81250	1.85770	1.67254	
0.57907	Hg	1.75276	1.77838	1.80298	1.81225	1.85741	1.67237	1.9507
0.58926	Na	1.75161	1.77719	1.80174	1.81098	1.85597		
0.64385	Cd	1.74643	1.77181	1.79619	1.80538	1.84986	1.66797	
0.65628	H	1.74546	1.77078	1.79513	1.80432	1.84866		
0.85212	Cs	1.73502	1.75993	1.78392	1.79301	1.83632		
0.89440	Cs	1.73358	1.75841	1.78237	1.79144	1.83462		
1.01398	Hg	1.73020	1.75491	1.77877	1.78783	1.83082	1.65626	1.9197
1.12866	Hg	1.72766	1.75229	1.77606	1.78514	1.82801	1.65438	1.9158
1.3622	Hg	1.72353	1.74806	1.77175	1.78078	1.82374		1.9101
1.39506	Hg	1.72311	1.74762	1.77128	1.78026	1.82331		
1.4695	Cs	1.72198	1.74649	1.77018				
1.517	Didy[e]	1.72132	1.74581	1.76955	1.77854	1.82167		
1.52952	Hg	1.72111	1.74559	1.76921	1.77821	1.82142	1.64943	1.9071
1.681	Poly[f]	1.71892	1.74336	1.76698				
1.6932	Hg		1.74323		1.77583	1.81930	1.64765	
1.7092	Hg	1.71857	1.74298	1.76669	1.77557	1.81908		1.9044
1.81307	Hg	1.71704	1.74154	1.76506	1.77414		1.64635	
1.918	Didy	1.71537	1.73985	1.76340		1.81644		
1.97009	Hg	1.71479	1.73927	1.76274	1.77178		1.64459	1.9015
2.1526	TeB[g]	1.71202	1.73640	1.75995	1.76891	1.81361		1.8977
2.167	Poly	1.71186	1.73624	1.75976	1.76878			
2.2493	Hg	1.71062	1.73497					1.8966
2.3254	Hg	1.70935	1.73372	1.75723	1.76622		1.64042	
2.4374	TeB	1.70750	1.73184	1.75537	1.76437	1.81000		1.8941
2.5947	H_2O					1.80797		
2.6119	H_2O	1.70462	1.72901	1.75245	1.76121			
2.6685	H_2O					1.80680		
2.6738	H_2O	1.70336	1.72770	1.75126	1.76017			
2.7248	H_2O	1.70255	1.72677	1.75034				
2.735	SiO_2	1.70214	1.72652	1.75000				
2.7397	H_2O					1.80541		
3.2434	TeB	1.69184	1.71613	1.73965	1.74855			
3.2668	Poly	1.69116	1.71541	1.73896			1.62668	
3.3026	Poly	1.69032	1.71459	1.73809		1.79706		
3.4188	Poly						1.62398	
3.422	Poly	1.68755	1.71170	1.73533	1.74421	1.79490		
3.5070	Poly	1.68544	1.70964	1.73318	1.74218	1.79345	1.62243	
3.5564	TeB	1.68414	1.70838	1.73201	1.74086	1.79250		
3.7067	TeB	1.68010	1.70440	1.72797	1.73690	1.78968		
4.2247	H_2O		1.68847					
4.253	H_2O	1.66268	1.68711	1.71212				
4.2553	H_2O					1.77863		1.8597
4.258	H_2O				1.71989		1.60645	
5.138	Poly					1.75437		
5.3034	TeB					1.74956		
5.343	Poly					1.74805		

[a] Barium titanium silicate glass—NBS data.
[b] Barium titanium germanate glass—NBS data.
[c] Calcium aluminate glass—NBS data.
[d] Tellurite glass—Eastman Kodak data.
[e] Didymium.
[f] Polystyrene.
[g] 1,2,4,trichlorobenzene.

Table III. Sellmeier Coefficients of Experimental Glasses

Melt number	F40	F52	F53	F110	F998
A_1	1.058985	1.042879	1.0862603	1.4069616	1.3100200
A_2	0.912350	1.013832	1.0539325	0.7645296	1.0088036
A_3	1.137683	1.468522	2.0163678	1.5310273	1.9148552
λ_1^2	0.0030489	0.0012197	0.0003761	0.0055175	0.0063054
λ_2^2	0.0315103	0.0316516	0.032435	0.0362642	0.0326582
λ_3^2	116.99181	144.58456	190.93270	147.23650	235.40295
λ_1	0.0552168	0.0349236	0.0193921	0.0742800	0.0794068
λ_2	0.1775114	0.1779091	0.1800973	0.1904317	0.1807158
λ_3	10.816275	12.024332	13.817840	12.134105	15.342847

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On the Twelfth day of Christmas, OSA sent to me,
Twelve motions moving, eleven new directors,
Ten agents snooping, nine teachers teaching,
Eight committees meeting, seven speakers speaking,
Six staff consultants, five memoranda,
Four long agenda, three back issues, two questionnaires,
And a by-law in a pear tree.

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Conference on Interference and Coherence Sydney, Australia, 24–25 August 1964

Provisional Subjects to be covered at a short ICO-AAS Conference on Interference and Coherence to be held preceding the conference in Tokyo and Kyoto (1–8 September 1964) include applications of interferometry to length standards and measurements, testing of optical systems, studies of the properties of materials, and to radio astronomy; new techniques in interferometry and new types of interferometers; and coherence and correlations. Both invited lectures and short papers on these topics are planned.

Provisional Timetable: Reunions at private homes on 23 August; conference sessions in Sydney University on 24 and 25 August; visits to National Standards and Radiophysics Laboratories, Sydney University, and University of New South Wales on 26 August; visits to scientific installations outside Sydney 27–29 August either as tours or by private arrangement made at the conference. OSA's Around-the-World Group Flight provides transport to this and the Tokyo meeting.

Scientific Tours could include visits to Narrabri, a country town 565 km north of Sydney, where there is an intensity interferometer for measuring stellar diameters and a radioheliograph for mapping the sun; Parkes, a country town 400 km west of Sydney and the site of a large radio telescope; Canberra, the national capital, 320 km south of Sydney (enroute to Melbourne) and the home of the Australian National University and Mount Stromlo Observatory; and Melbourne, capital of State of Victoria, the location of CSIRO Division of Physical Chemistry, the University of Melbourne, and Monash University.

Accommodations can be arranged at one of the University Colleges either for the conference only or for the full week at £A2.12.6 ($7.00) a day including meals.

Registration fee will be £A4 ($9.00) including the conference dinner. Students may register for the meeting only for £A1 ($2.20). Tours will be extra.

Additional Information can be obtained from the Australian National Committee for Optics, W. H. Steel, Convenor, CSIRO Division of Physics, City Road, Chippendale, N.S.W., Australia.

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An 8–14 Micron Infrared Astronomical Photometer

James A. Westphal, Bruce C. Murray, and Dowell E. Martz

A system for measurement of 8–14 μ infrared emission from extra-terrestrial objects is described. The photometric system utilizes a mercury-doped germanium detector cooled to liquid hydrogen temperature to achieve increased sensitivity in this spectral region. A method is presented for minimizing the problem of atmospheric and component emission. The system has been used to measure the radiation from the star α Orionis, from the unilluminated moon, and from several planets.

Introduction

Since gaseous constituents of the earth's atmosphere absorb strongly at a number of wavelength intervals throughout the electromagnetic spectrum, measurements of the radiation emitted by extra-terrestrial objects performed at the surface of the earth must necessarily be confined to those spectral regions known as atmospheric "windows." Conventional astronomy has been conducted largely in the visible "window" with extensions by photoelectric photometry into the edges of the ultraviolet and near infrared regions. Fairly recently techniques permitting greater utilization of the 3–5 μ atmospheric window have become available and work is progressing in this area.[1] With the exception of work by Sinton *et al.*,[2] however, only limited efforts have been made in recent years toward improving the measurements in the 8–14 μ window, due to the lack of sensitive detectors and to the severe restrictions imposed by environmental emission.

Further knowledge of the amount of radiation in the 8–14 μ interval emitted by the moon, planets, and stars is of special interest to astronomers. For the colder objects such as the darkened moon and the more distant planets this spectral region represents the only interval in which significant quantities of radiation are emitted. For the warmer planets and for stellar sources, this information, coupled with measurements at shorter wavelengths, provides further clues concerning the nature of planetary and stellar atmospheres.

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At wavelengths shorter than about 5 μ the earth's atmosphere acts only as an absorbing and scattering medium which serves to reduce the energy available from an external source. However, as one approaches the 8–14 μ interval, emission by the atmospheric constituents becomes increasingly important. The emission spectrum of atmospheric gases has been studied by Goody[3] and by Bell *et al.*[4] Figure 1 shows the 8–14 μ sky radiance at various elevation angles as measured at Mt. Wilson. The total energy radiated in the 8–14 μ window is sufficient to produce a sky radiance many times that of the fainter external source to be measured. In addition, the telescope and photometer components within the field of view are even more intense sources of radiation. Essentially, the problem of photometry in this spectral region is equivalent to that which would be encountered in conducting stellar measurements in the visible region against a daytime sky while using a telescope constructed from luminescent materials.

Figure 2 shows the spectral transmittance in the 8–13 μ interval of the earth's atmosphere, obtained by Sinton and Strong[5] at Palomar by square-root law extrapolation of data from several elevation angles. The strong absorption defining the edges of the atmospheric window is due to water vapor and, to a lesser extent, carbon dioxide. Since the concentrations of both of these atmospheric constituents are strongly dependent on elevation, transmittance and radiance are strongly altitude-dependent.

This paper discusses the techniques used in the construction and operation of an 8–14 μ infrared telescope utilizing quantum detectors recently developed[6] for this spectral region rather than the conventional, less sensitive thermal detectors. The increased responsivity of these detectors, the use of special interference filters and cooled optical baffles, and operation

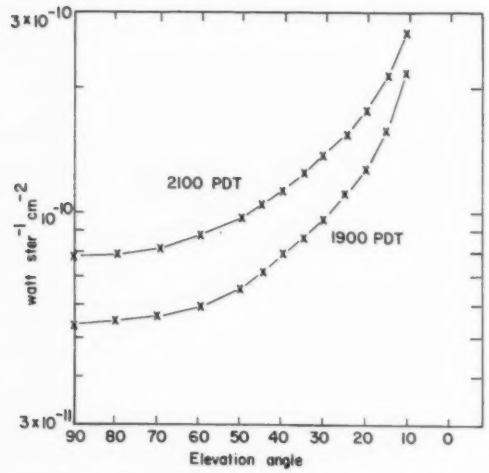

Fig. 1. The spectral radiation of a clear sky for several angles of elevation above the horizon, measured at Mt. Wilson, California, September 20, 1962.

of the system at a high altitude observing site have resulted in a significant increase in over-all signal-to-noise ratio. Details of measurements obtained at a White Mountain, California, site during the summer of 1962 will be reported in another paper now in preparation.

Telescope and Photometer

Since the peak emission from objects at room temperature occurs at about 9.6 μ, it is necessary that the amount of extraneous background radiation on the cell be reduced to a minimum. The total power radiated in the 8–14 μ interval from low-emissivity components such as mirrors, lenses, and windows is significant, and a careful choice of materials for the optical system is of importance. The emissivity of evaporated gold is the lowest ($\sim 1\%$ at 10 μ) of any common metal[7] and has been used on all mirrors in the system. Only one window, that on the cell dewar, was employed, and this along with the Fabry lens in the cooled collimating baffle was constructed from barium fluoride (BaF_2). The physical properties of BaF_2[8] have proved to be superior to those of other materials tried, including KRS-5 and Irtran II.

To permit operation at the high altitude site, a semi-portable telescope was constructed in the CIT Central Shops utilizing a 50.8-cm diameter paraboloid loaned by the Mt. Wilson and Palomar Observatories. A convex secondary and a flat mirror were used to bring the $f/15$ optical beam coincident with the declination axis of the German mounting system. The telescope and instrumentation were installed in a concrete block building located near the Barcroft Laboratory of the White Mountain Research Station near Big Pine, California. The elevation at this site is about 3900 m (12,800 ft).

The optical path followed by the $f/15$ beam is illustrated in Fig. 3. The working component of the photometer was a rotating chopper mounted at a 45° angle to the incoming beam. In order to suppress the unwanted background radiation from the sky as well as that from the optical components within the field of view, the total energy from the background plus object was reflected into the cell during the first half-cycle while the chopper blade was in the closed position. As the chopper rotated into the open position during the next half-cycle, radiation from an adjacent portion of the sky was reflected into the cell by a fixed comparison mirror located at the same 45° angle but slightly below the chopper blade. The ac output of the cell represents background plus object minus background, or to a good approximation, that due to the object alone. For planetary objects the spacing between the measuring beam and the reference beam is about 5 min of arc. Good correlation between the two beams was usually observed under this condition; although, the null signal from a uniform sky nevertheless displayed some low-frequency drift. A spacing which provided 20 min of arc separation between the two beams was necessary for lunar observations, which resulted in some increase in background noise.

Detector and Cooling Dewar

Although several detectors of the doped germanium type meet the minimum sensitivity requirements for an 8–14 μ infrared telescope system, mercury-doped germanium (Ge–Hg) was selected over the more common varieties for two important reasons. First, the long wavelength cutoff for Ge–Hg coincides closely with the useful upper limit of the 8–14 μ atmospheric window, thus eliminating the need for special cutoff filters to

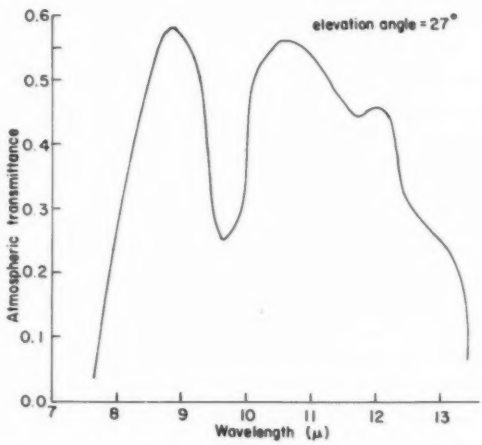

Fig. 2. The spectral transmission at Palomar after Sinton and Strong.[5]

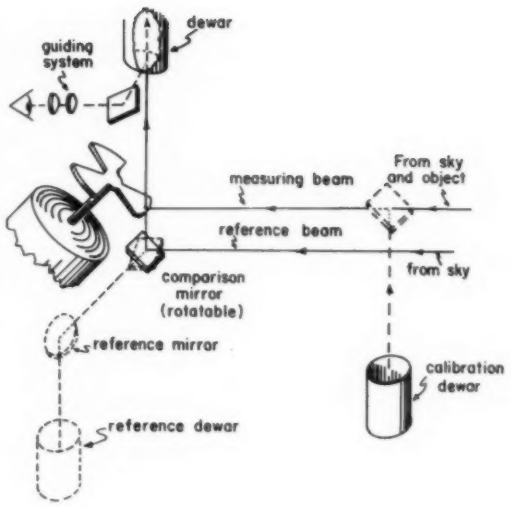

Fig. 3. The optical paths followed by the measuring and reference beams through the photometer.

block the strong atmospheric emission beyond 14 μ. Secondly, the wider ionization energy gap of Ge–Hg makes it possible to achieve adequate cell resistance and sensitivity using liquid hydrogen as the coolant rather than liquid helium, a distinct advantage in the type of field operation for which the system was designed.

Two 2 × 2 mm Ge–Hg crystals, manufactured by Texas Instruments, Inc., and supplied to us by the Naval Ordnance Test Station, China Lake, California, were mounted in two modified Linde LNI-28 dewars as shown in Fig. 4. The dewars are designed for use with either liquid helium or hydrogen using liquid nitrogen shielding. Modifications included a 12.7-cm window extension to provide space for a special baffle system which limited the detector field of view to about $f/15$. As indicated in Fig. 5, the converging $f/15$ beam from the telescope was brought to a focus at the entrance aperture located on the front surface of the dewar window. This room temperature aperture was an elliptically shaped hole sandblasted in a microscope slide cover glass and mounted at a 15° angle to the optical axis, providing effectively a 1-mm diam circular aperture. The surface surrounding the aperture was aluminized to reflect the star or planet image into a guiding eyepiece system when the image did not fall completely within the aperture.

After leaving the focal plane, the diverging optical beam passed first through the 0.5-mm thick BaF_2 window, then through a series of cooled baffles in thermal contact with the liquid hydrogen heat sink. These cooled baffles effectively removed most of the stray radiation outside the $f/15$ cone. An interference type optical filter with a cut-on at 8.2 μ was also located within the cooled radiation shield. Finally, a 9-mm diam BaF_2 Fabry lens was used to refocus the divergent beam on the sensitive area of the detector, forming a real image of the primary mirror.

Operated in this manner the detector had an angular field of view of about 10^{-3} steradians with the enclosing radiation shield cooled to liquid hydrogen temperature. Under these conditions the resistance of the Ge–Hg crystals was about 1 MΩ at sea level. However, as the ambient pressure on the liquid hydrogen was reduced by moving to higher elevations, the resistance of the detectors increased markedly, reaching 8.0 MΩ at the 3900-m site on White Mountain. Although cell resistance was remarkably constant at a given altitude, it was necessary to determine cell operating parameters such as bias current at the observing site.

Another property of these detectors that had not been expected was a noticeable increase in response at very low frequencies. The normal photoconductive time constant of these detectors is of the order of 1 μsec. However, at modulation frequencies below 200 cps it was observed that additional response with a very long time constant began to appear. This is possibly explained as an added bolometer effect due to actual temperature changes in the crystal produced by absorbed radiation, an effect which is especially apparent under the nearly complete radiation shielding used here. The effect is even more pronounced because operation with liquid hydrogen places the Ge–Hg detector on the knee of the resistance versus temperature curve.

Although the dewar has been designed for a holding time of several hours with liquid helium, there are several advantages in being able to use liquid hydrogen as the cooling medium. The holding time with liquid hydrogen averaged about 80 hr in the LNI-28 dewar,

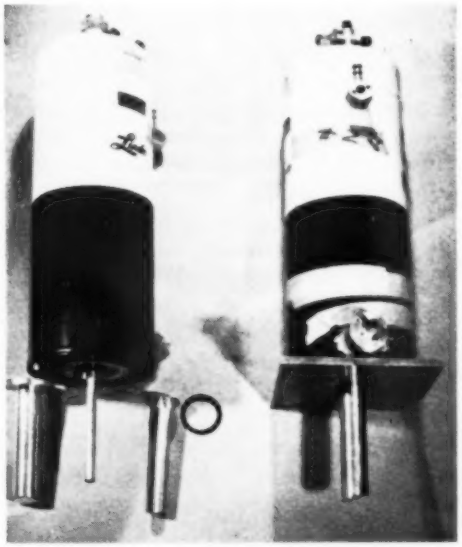

Fig. 4. Photograph of the modified Linde LNI-28 dewars showing the window extension and radiation shield.

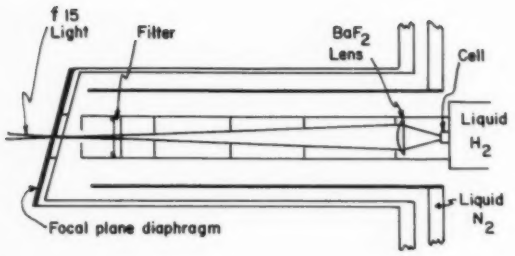

Fig. 5. Diagram of the aperture and cooled radiation shield.

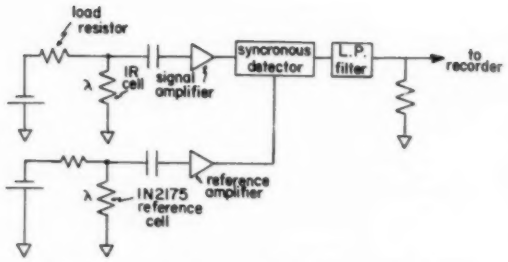

Fig. 6. Schematic diagram of the electronic circuitry.

completely eliminating the need for refilling during an all-night observation run. In addition, the comparative ease with which liquid hydrogen can be handled and stored, coupled with relatively low cost, are added benefits. A further increase in Ge–Hg detector sensitivity might, in principle, be realized by using liquid helium, but the very high resistance obtained (hundreds of megohms) under such complete radiation shielding leads to serious difficulties in the electronic circuitry. A noise equivalent power approaching 2×10^{-12} W has been achieved in practice. The corresponding detectivity D^* (273°K, 180, 1) approaches 5×10^{10} cm(eps)$^{1/2}$/W for the 8.5–13.5 μ wavelength interval.

Electronics

As indicated in Fig. 6, the Ge–Hg detector was connected in series with a load resistor of several megohms to a battery bias supply. The chopped radiation incident on the cell causes a variation in resistance which in turn produces a small ac voltage at the modulation frequency. This signal was amplified by a low-noise amplified (Infrared Industries Model 600 tuneable microvoltmeter) and fed into a special autocorrelation detector network. A small lamp and silicon photocell mounted near the chopper were used to produce a square-wave reference signal phase locked to the chopper and, hence, to the ac signal from the infrared detector. This square-wave signal was used to switch a four transistor synchronous detection network of the type described by Smith *et al.*[9] The overall bandwidth of the system was controlled by a simple lowpass filter at the output. A recorder (Sargent Model MR) with a mechanical integration device attached to the pen allowed the signal to be recorded at a bandwidth of about 1 cps with the possibility of deriving narrower bandwidth from the chart by direct integration.

Calibration

For calibration purposes a set of auxillary mirrors was incorporated into the photometer. At the beginning, and at various times during an observation period, a calibration procedure was followed which consisted of measuring the signal produced by alternately viewing two blackbodies at different temperatures. These blackbodies were blackened-metal cavities in thermal contact with liquids of known temperature (usually ice water and liquid nitrogen) contained in a standard glass dewars.

To view one of the blackbodies, a mirror was inserted into the measuring beam path as shown in Fig. 3. The second source was viewed in the reference beam by rotating the comparison mirror 180° and using a second mirror to reflect the optical path down into the blackbody. Since two reflecting mirrors were used in each path, the signal generated represented the difference in radiant power emitted by the two blackbody surfaces. This was computed directly from the Planck radiation law assuming unit emissivity of the calibration sources.

Operation

The system described has performed successfully over a period of several months at a high altitude observing site on White Mountain. Normal procedure for planetary and stellar observation has been to balance the reference and measuring beams closely with the telescope trained on the sky near the object. Once a noise level trace has been established, the telescope was moved on the object and maintained there by occasional small adjustments in the slow motion guidance. The operator's view through the guiding eyepiece of the focal plane image as reflected by the aluminized aperture gave absolute evidence that the radiation from the object was falling on the detector.

It was observed that fluctuations in the emitted sky radiation collected by the two beams was usually the limiting factor in length of time a faint source could be observed. Such fluctuations are probably caused by slight differences in emission of the air masses viewed by the two beams as evidenced by slow random drifts of the recorder pen. When both beams are trained on the sky on a few clear nights with moderate winds, the turbulence in the atmosphere was a severe problem and occasionally made it necessary to suspend operation. Usually conditions were best in the early morning hours from midnight to sunrise. The daylight hours at the White Mountain site are often characterized by rapid cloud formation as the relatively moist air from the Owens Valley is forced over the summit by the prevailing westerly winds. Under these conditions

and even when the clouds were not actually visible, the sky noise was extremely high. A combination of sky fluctuations, optical surface temperature variations, and variations in the cell responsivity due to changes in pressure on the liquid hydrogen, combined to limit the minimum detectable temperature of this system under good conditions to about 105°K for an extended object outside the atmosphere.

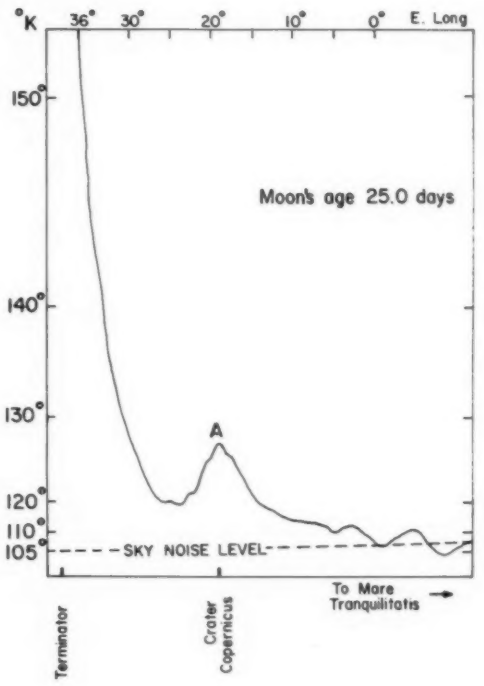

Fig. 7. Recorded signal obtained as the telescope was traversed across the dark portion of the moon at 1119 UT 25 August 1962. The traverse began at the terminator in the vicinity of crater Kepler and extended to near Mare Tranquilitatus. The warm area shown at A is associated with the crater Copernicus.

In the case of the moon, where a position reference is required for data reduction, a photograph of that object superposed on a reference reticule pattern was obtained through a low-power telescope attached to the main telescope tube.

Performance

Although a full discussion of the measurements obtained with this system will be presented in a later paper, a brief summary of the results will illustrate the nature of the data. Figure 7 shows the recorded output as the telescope was traversed across the moon at 1119 UT, 25 August 1962. The observed peak at "A" indicates an area definitely warmer than its surroundings and is possibly due to the presence of bare rock surfaces in the vicinity of Copernicus. The geographic resolution of the system is about equivalent to a circular area 50-km diam at the surface of the moon. Several of these relatively warm areas have been recorded and further study is being conducted.

An average of several measurements of Jupiter has yielded an effective temperature of 128°K at a signal-to-noise ratio of about 10:1 for a one-second observation time. A measurement of the star α Orionis (Betelgeuse) yielded a signal-to-noise ratio of 3:1 for the same observation time.

The authors wish to express their appreciation to the Naval Ordnance Test Station, China Lake, for valuable technical assistance and support, and to the University of California personnel who manage and operate the White Mountain Research Station. We gratefully acknowledge in addition the many helpful suggestions contributed by I. S. Bowen, of the Mt. Wilson and Palomar Observatories, by R. L. Wildey and E. V. Nenow of CIT, and by R. E. Wilson and B. J. Gorrano of NOTS. This work has been supported by Grant NSF-G 25210 from the National Science Foundation and Grant NsG 56–60 from the National Aeronautics and Space Administration.

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Dr. W. L. Hyde *USA*, Miss A. Fiorentini *Italy*, Professor and Mrs. R. W. Ditchburn *England*, and Professor and Mrs. Stanley S. Ballard *USA*.

Books *continued from page 740*

interest. Due to the limitation of the technique to the low-lying vibrational states having a reasonable population at convenient temperatures, we are not often able to acquire sufficient data concerning the effect of changes in vibrational quantum numbers on the moments of inertia of the molecule and to extrapolate to the vibrationless equilibrium state. Therefore, the accuracy in determination of internuclear distances is often not better than $\pm$ 0.01 Å, rather than the $\pm$ 0.001 Å that many workers used to think they were achieving. Wilson's critical examination of this situation may serve as a warning against precipitate conclusions with respect to changes in bond structures drawn from small variations of observed bond lengths.

Closely connected to the above topics is the paper presented by W. Maier *Freiburg i. Br.*, surveying progress and results in the microwave spectroscopy of gases obtained in 1959 and 1960. In the experimental part, the performances of a microwave spectrometer with regard to sensitivity, resolution, and accuracy of frequency determination are discussed: recent improvements, particularly of the Stark modulation spectrometer and of maser spectrometers, are reported. Results obtained by microwave methods are summarized in a number of well-computed tables dealing with structural parameters, potential barriers, equilibrium configurations of rotational isomers, and dipole moments of a large number of molecules investigated in the last years. Especially valuable is an extensive bibliography covering 239 research papers published in 1959, 1960, and early 1961.

Two lectures are dedicated to electron spin resonance spectra. G. K. Fraenkel *Columbia University* reports on the theory of carbon-13 splittings in such spectra arising from the interaction of the unpaired electron with ^{13}C nuclei in π-electron radicals. The comparison of experimentally observed and calculated splittings given in Table 7 are in surprisingly good agreement. A discussion of characteristic hydrogen hyperfine couplings in aliphatic free radicals is presented by D. H. Whiffen *NPL*, who emphasizes the particular value of such studies for the differentiation of α-hydrogen atoms attached directly to a free radical carbon from β-hydrogens attached to it through an intermediate atom.

Nuclear magnetic resonance is presented by R. E. Richards *Oxford*, who deals with the chemical applications of NMR spectroscopy and gives special attention to the directions in which the subject may develop in the next few years.

Most of the papers presented at the Amsterdam meeting belong to the "classical" fields of ultraviolet, infrared, and Raman spectroscopy: within the restricted scope of this review, only brief references will be given. H. Hartmann *Frankfurt*, deals with new concepts in the theory of π-electron spectra. Within the framework of the one-electron treatment and starting from a modified Hueckel theory that takes into account higher single electron atom states, Hartmann attempts an interpretation of spectra of π-electron systems. In the case of a number of polycyclic aromatic hydrocarbons, his approach leads to an understanding of Scheibe's empirical rule that implies in the formulation of Dr. Hartmann a constant energy separation between the first excited singlet state and the ionization potential of the molecules in this group. As is nearly always the case in his well-known work, the author aims primarily at a fundamental, qualitative understanding of electronic molecular energy levels through simple concepts; applying his theory to the calculation of the resonance energies of naphthalene, anthracene, and phenanthrene, he arrives at a highly satisfactory agreement with the experimental values. G. Briegleb *Wuerzburg* presents an ample and well-documented paper on charge-transfer spectra of neutral molecular complexes, giving special attention to compounds of iodine with organic donor molecules. T. Foerster *Stuttgart* studies the electronic absorption spectra of weakly coupled molecules and arrives at an interpretation of the spectral changes observed, e.g., on solutions of organic dyestuffs in varying concentrations, by considering the splitting of the electronic states and the resulting selection rules for dimeric forms and higher associations. In his lecture on vacuum ultraviolet spectroscopy, G. Milazzo *Rome* examines the actual state of this field of research with respect to improvements in the experimental techniques and the chemical applications and results that have been obtained or which can be expected in the near future. G. Porter *Sheffield* reports some theoretical considerations on the possible mechanisms of energy tranfer from molecules in the triplet state.

The remaining seven lectures refer to vibration spectra. S. Brodersen *Aarhus University* scrutinizes some of the principal problems in the determination of the potential function, a subject of outstanding importance for the interpretation of infrared and Raman spectra by vibrational analysis. In fact, questions concerning the uncertainty in the definition of the harmonic potential, the neglect of anharmonic terms, the frequent applicability of distinctly different force field models reproducing the observed frequencies with equivalent consistency, the choice and meaning of significant interaction constants, and the transferability of the calculated potential constants to similar molecules are familiar to all workers in the field and constantly bring about doubts and worries. This reviewer would have liked a more circumstantial treatment of some of the alluded points only touched upon in Brodersen's paper.

M.-L. Josien *Paris* presents a study of molecular interactions in liquids by infrared methods, considering especially solute-solvent interactions and their influence on the frequency, intensity, and band contours of the stretching mode of the carbonyl group. The lecture of G. C. Pimentel *Berkeley* on matrix technique and its application in the field of chemical physics emphasizes the infrared spectroscopic detection of extremely reactive molecules and radicals, such as HNO, HCO, NH, and iso-N_2O_4, dispersed in a spectroscopically distinct host lattice at low temperatures. N. Sheppard *Cambridge University* reports on some studies of physical and chemical absorption by means of infrared spectroscopy. The first phenomenon is illustrated from spectra of H_2, CH_4, NH_3, CH_3Br, and other molecules adsorbed on porous silicate glass; in the field of chemisorption, infrared spectra are presented that have been obtained from simple aliphatic compounds adsorbed on small metal particles supported by silica.

Two papers deal with intensity problems in Raman spectra: H. J. Bernstein *NRC* gives an analysis of the problems arising in converting the observed Raman intensity in the liquid phase to the true intensity, relating the latter quantity to the form of the polarizability curve as a function of internuclear distance. The different effects which lead in the liquid phase to the modification of the intensity obtained in the gaseous state are separated. P. P. Shorygin *Moscow* presents a discussion on the resonance Raman effect taking into account the dependence of the maximum electronic-absorption frequency upon the nuclear coordinate, which has been disregarded in Placzek's polarizability model. In a lecture on long-wave Raman spectroscopy, the writer of this review presents a discussion of the experimental techniques used for the excitation of Raman spectra in the red and near-infrared region of the spectrum and of some recent results obtained by means of these methods.

The rapidly broadening field of molecular spectroscopy, with respect both to the physical principles involved and to their application to the elucidation of chemical problems, is well represented by the diversity of the topics discussed at the Amsterdam meeting. The book offers plenty of stimulating hints and helpful advice for all workers engaged in research in this area.

H. Stammreich

Brighter Spectrographic Images by the Use of Anamorphic Optics

E. Eisner

A new method is proposed for increasing the light per unit area in a spectrographic image for a source of given surface brightness (luminance) and for a given linear dispersion. An imaging system is used that has a shorter effective focal length and a larger relative aperture in a plane parallel to the slit than in a plane containing the direction of dispersion. In favorable cases, twentyfold intensification would be possible. Relations are derived to enable the sizes and focal lengths of the components needed for one such system to be calculated simply in any particular case. The quality of the components required is not critical.

It has previously been suggested[1] that a cylindrical lens may be placed in front of the plate of a photographic spectrograph to reduce the height (parallel to the slit) of the spectrum and thereby to increase the photographic brightness. This method has the disadvantage that the line produced on the photographic plate when the slit is monochromatically illuminated is not an image of the slit, that is, that stigmatism is completely lost. Therefore, unless the image of the slit in the absence of a cylindrical lens were precisely a straight line and unless the image were precisely normal to the dispersion direction, spectral resolution would be reduced by the cylindrical lens. Also, one could not take several spectra simultaneously from different parts of the slit except by having a correctly placed cylindrical lens for each spectrum. Further, for certain uses of spectrographs, for instance for topographic interferometry,[2] stigmatism is an essential property. The greatest gain in intensity with this arrangement is achieved when the cylindrical lens is made to "image" the exit pupil of the spectrograph (usually the telescope objective in prism spectrographs) on the plate. The length of the bright line on the plate is, therefore, independent of the length of the slit, and the maximum gain of intensity occurs only when the slit is long enough to fill the height of the cylindrical lens with light. If the slit is made shorter than this, the intensity of the spectral line falls, unless the cylindrical lens is replaced by another whose focal length is shorter in proportion to the slit length. This is clearly an inconvenient arrangement.

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However, if we replace the rotationally symmetrical telescope lens and the cylindrical lens by an anamorphic lens, we can produce a spectrum of reduced height that is still a stigmatic image of the slit. It can readily be shown that the gain of intensity produced by such a system of appropriate design is approximately equal to the ratio of the numerical aperture of the anamorphic lens in the plane parallel to the length of the slit to its numerical aperture in the plane containing the the direction of the dispersion. Thus, to obtain a large intensification, we need an anamorphic lens of large magnification ratio and large numerical aperture. It will not usually be necessary for the resolution to be as good in the direction of large numerical aperture (since this is normal to the dispersion direction) as in the perpendicular direction; and it may not be necessary for the anamorphic lens to be achromatic. Further, it is not necessary for the lens system to be capable of working for more than one pair of conjugates. For these reasons the anamorphic lenses used in kinematography are not well suited to this purpose.

Buchele and Goossens[3] have described an anamorphic system for Schlieren photography that is well suited for adaptation to this spectrographic application. This system (Fig. 1) would use three cylindrical converging lenses, L_2, L_3, L_4, with their cylindrical axes parallel to the direction of dispersion. The first of these, L_2, is placed near (position not critical) the telescope objective (or other producer of the spectrographic image) L_1, and uses the image I_1 produced by L_1 as a virtual object. L_2 produces a real "image" I_2 at some point between L_2 and I_1. I_2 is not, of course, a true image of the slit, since the cylindrical lenses produce no convergence perpendicular to the slit; what is meant here is that all strip elements of L_1 parallel to the slit would

produce, with L_2, images of the slit in the plane of I_2. We shall call "images" like I_2 "pseudoimages".

I_2 is now relayed by lens L_4 into the plane of I_1 where a true, erect, anamorphic image I_4 of the slit is produced. The lens L_3 is a field lens, placed approximately at the position of the pseudoimage I_2; it "images" L_2 on L_4 and reduces the aperture needed in L_4 to ensure collection of all the light. We shall continue the discussion in terms of lenses, but all the optical processes described could be carried out with mirrors.

Let us use the notation of Fig. 1, together with the following definitions:

D_n is the dimension of lens L_n in a direction parallel to the slit;

l_n is the length, in a direction parallel to the slit, of the image or pseudoimage produced by lens L_n;

$\Phi_n = \dfrac{l_n}{V_n}$ is the angular height of field required of lens L_n;

$R_n = \dfrac{D_n}{V_n}$ is the relative aperture required, on the image side, of lens L_n;

M_n is the "magnification" produced by lens L_n;

$M = M_2M_4$ is the total magnification produced by L_2 and L_4 in combination (L_3, being a field lens, does not affect the size of the image).

M_3, M_4, and M will, in our arrangement, be negative; M_2 will be positive; M_2, M_4, and M will be numerically less than one. The image intensification produced by using the cylindrical lenses will be $(-1/M)$ if there is no loss of light by reflection, absorption, or scattering and if the spectral resolution is not significantly reduced.

Assuming all lenses to be thin and L_1 and L_2 to coincide, the following relations can be shown to hold:

$$\frac{R_2}{R_1} = \frac{1}{M_2}, \tag{1}$$

$$\frac{R_4}{R_1} = -\frac{1}{M}, \tag{2}$$

$$\frac{\Phi_2}{\Phi_1} = 1, \tag{3}$$

$$\frac{\Phi_4}{\Phi_1} = \frac{M(1 - M_4)}{M_4 - M}. \tag{4}$$

Suppose we have a spectrograph that, without cylindrical lenses, has an image relative aperture R_1. Then the greatest intensification we can get in the image is governed by the highest relative aperture (R_4) of a cylindrical lens of acceptable quality that we can use for L_4. From Eq. (2), we see that if, in a typical case, the spectrograph were originally of relative aperture $1/20$, we could obtain a tenfold intensification if L_4 could be of relative aperture $1/2$. This aperture requirement in L_4 is not as severe as it looks, since aberrations in this lens would cause mainly astigmatism parallel to the slit in the final image. Also, the large dimension of the final polychromatic image is the spectrum length, and this is parallel to the cylindrical axis of L_4.

Having fixed R_1 and Φ_1 by the properties of the spectrograph whose image is to be intensified, and M by the intensification we wish to achieve, we are still free to choose M_2 or M_4, i.e., to distribute the image reduction between L_2 and L_4.

It can be seen from the above relations that, if the image reduction is done mainly by one of the lenses L_2 or L_4, then that lens must have a large relative aperture and also subtend a large field angle. The way the reduction should be split between the lenses will depend on the way the aberrations vary with the two variables R and Φ. If we do not know this variation, we may compromise by splitting the reduction equally between L_2 and L_4, that is, by making

$$M_4 = -\sqrt{-M}. \tag{5}$$

Having determined the magnifications, the positions of the lenses are determined, and their focal lengths follow from the lens formulae.

$$\frac{F_2}{F_1} = \frac{M}{M_4 - M}, \tag{6a}$$

$$D_2 = D_1, \tag{6b}$$

$$\frac{F_3}{F_1} = \frac{M(M_4 - M)}{M_4^2(1 - M)}, \tag{7a}$$

$$D_3 = \frac{M}{M_4} l_1, \tag{7b}$$

$$\frac{F_4}{F_1} = \frac{M - M_4}{(1 - M_4)^2}, \tag{8a}$$

$$\frac{D_4}{D_1} = \frac{M_4 - M}{M(1 - M_4)}, \tag{8b}$$

$$\frac{V_2}{F_1} = \frac{M}{M_4}, \tag{9a}$$

$$\frac{V_4}{F_1} = \frac{M - M_4}{1 - M_4}. \tag{9b}$$

It would probably not be necessary for any of the cylindrical lenses to be achromatic as long as the dispersion were not too great; for widely different colors will fall on different parts of the length of L_4, so that a small rotation of this lens about an axis parallel to the slit could bring all the images nearly onto the correct surface.

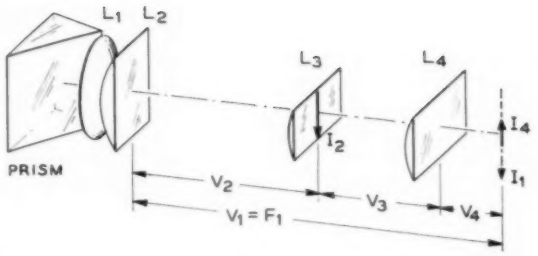

Fig. 1. Disposition and relative sizes of the lenses for $R_1 = 1/4$ $\Phi_1 = 1/4$, $M = -1/4$, $M_4 = -1/2$ (spectrograph slit vertical)

If a lens system of this kind were introduced into the collimator as well as into the telescope and if the condenser filled the lenses with light, the same intensification could be achieved without reduction in the height of the spectrum.

Anamorphic systems in spectrographs are likely to be useful for image intensification when the dispersion required is fixed by external considerations (e.g., photographic grainsize), and cost, weight or freedom from aberration limit the circular numerical aperture that can be used.

I would like to thank J. S. Courtney-Pratt for helpful discussion and, in particular, for drawing my attention to the paper by Buchele and Goossens.[3]

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OPTICISTS

Sir Gordon Sutherland *National Physical Laboratory* and Dr. C. J. Humphreys *NOL—Corona*, consider a question of optics during the International Symposium on Molecular Structure and Spectroscopy held in Tokyo, September 1962. Dr. Humphreys is the co-author of a paper in this issue—see page 691.

Dr. M. K. Wilson *Tufts*, Dr. and Mrs. George Harrison *MIT*, and Mrs. Richard C. Lord at one of the receptions in Tokyo held during the International Symposium on Molecular Structure and Spectroscopy, September 1962. The characteristic back and elbow of the OSA President-Elect may be seen on the extreme right.

Applied Optics

Letters to the Editor

Letters to the Editor should be addressed to the Editor, APPLIED OPTICS, 1155 16th St., N.W., Washington 6, D.C.

A Graphite Resistor Source for Image Furnace Research

E. E. Maust, Jr., and W. E. Warnke

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Received 14 March 1963.

The Bureau of Mines is engaged in a research program directed toward the improvement and development of nonmetallic refractory materials. One of the tools to be used in this work is a 152-cm double-paraboloidal mirror-image furnace. As with most image furnaces, its characteristic feature is the high irradiance obtainable over a relatively small area of the focal plane of the image mirror when a suitable high-temperature source is placed at the focus of the other mirror. The first source used in this furnace was a high-current carbon arc of the type used in the 152-cm searchlight. A calorimetric investigation was made using this source and a water-flow calorimeter placed behind various apertures lying in the focal plane of the image mirror. The results of this investigation indicated a variation of irradiance with time, due to arc fluctuations, and a Gaussian distribution of irradiance in the focal plane, as observed by other investigators.[1,2]

Owing to the difficulty of accurately characterizing the high-current carbon arc in terms of the parameters required for a theoretical analysis of furnace operation, calorimetric data for this source alone did not constitute sufficient information to ascertain the origin of the Gaussian distribution of irradiance at the image. There was a need for a uniform source that could be precisely described in terms of size, shape, temperature, and emissivity, and could be easily controlled. Calorimetric measurements of the irradiance obtained from such a source might indicate the origin of the distribution of irradiance observed using the arc source and, in addition, would provide a basis for predicting the performance of any other source in this optical system.

Consideration of the methods and materials suitable for obtaining a stable and controllable high-temperature source indicated that an electrical resistance element of graphite had great promise. However, protecting such an element from oxidation at high temperatures, without incurring undue losses of radiant energy, is a formidable problem. The method finally adopted is unique in that no solid material is interposed between the source and the source mirror, although the furnace is still operated open to the atmosphere.

As shown in Fig. 1, the over-all shape of the graphite element is that of a truncated cone with cylindrical projections on opposite ends of a basal diameter. These projections are forced into water-cooled copper connecting blocks to which the electrical leads are attached when the source is operated. The truncated body of the element is cut and shaped in such a manner that the thin 19-mm diameter disk at the top is the only electrical connection between the copper connecting blocks.

The resistor mounting is designed so that the face of the resistor disk is the only hot part of the source that can radiate to the source mirror, the remainder of the element being totally enclosed by a water-cooled copper jacket. This jacket is shown removed in Fig. 1. When placed in the furnace, the face of the disk is made coincident with the focal plane of the source mirror. In addition to confining the effective source to a disk, the jacket permits the maintenance of an inert gas atmosphere around all hot parts of the resistor by means of a flow of gas through the jacket. The gas enters through an opening (not visible in Fig. 1) in the mounting board behind the resistor and exits through the very narrow annular space between the disk and jacket when the latter is in place. The gas emerges at high velocity, and because of the contour of the interior of the jacket, is directed so that it converges to a point about 2.5 cm in front of the disk, thereby forming a protective cone of inert gas. A second gas channel is built into the jacket and is so designed that another slightly larger cone of gas is formed around the first. The two directed gas-flows result in a complete gas envelope around the face of the resistor disk without any physical confinement of the gas and hence without any significant loss of radiation by absorption. At first, helium was used for both the inner and outer cones, but convection currents led to incomplete cone formation. Since then, argon has been used for the outer cone and helium for the inner cone; entirely satisfactory results have been obtained. Apparently, the heavier argon tends to contain the helium, and convective disruption of the envelope is prevented. The success of this design may be judged from the fact that the source has been operated continuously for periods exceeding four hours at temperatures above 2000°C with no visible signs of oxidation.

It is difficult to profile the thin graphite disk so as to obtain a uniform disk temperature from joule heating alone. The uniformity can be improved significantly by returning to the disk some of the radiation emitted from its back surface. This is accomplished by placing a metal reflector, of approximately the same area as the disk, immediately behind and parallel to its back surface. In the normal operating position for the source, the graphite disk is vertical, thus making it possible to suspend the reflector in the space behind the disk, using small tabs hooked over the edges of the main body of the element. The reflector carries no appreciable current and does not contact the disk. Radiation interchange between the metal reflector and the graphite disk, and the interchange between various regions of the disk via reflection from the polished surface of the metal tend to eliminate temperature gradients. By this means it was possible

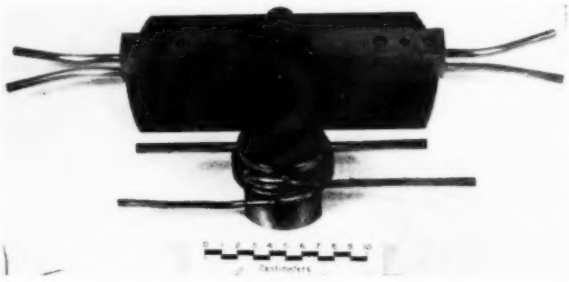

Fig. 1. A graphite resistor source.

to achieve a uniformity of surface temperature of ±30°C over the central 1-cm diam area of the disk, at 2300°C.

In the calorimetric investigation[3] uniformity of the source was the primary consideration; hence, the maximum operating temperatures were limited by the molybdenum reflector used. The passing of approximately 250 A through the resistance element gave a surface temperature of 2305°C. For the source at this temperature, the irradiance over a central 1-cm diam area of the image was found to be 21 cal/cm²-sec, and, within experimental error, was as uniform over this area as the radiant intensity of the source itself. The measured irradiance differed by only 2.5% from the irradiance calculated on the basis of a quantitative mathematical analysis of the furnace.[3] Thus, it was shown that for planar sources up to 1-cm in diameter in the focal plane of the source mirror, the distribution of irradiance at the image was identical to the distribution of radiant intensity of the source.

On the basis of these and other data,[3] it was concluded that the origin of the Gaussian distribution of irradiance observed using the high-current carbon arc source was not mirror imperfection or aberration due to using an extended source. It is apparently a characteristic of the arc.

Although the original objective of the development of the graphite resistor source was to ascertain the characteristics of an optical system, the image irradiance obtainable with it is sufficiently high to render it a practical source for some types of image furnace research work. The ease of control and constancy with time further enhance its usefulness for applications which do not require the highest irradiances.

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A Method for Measuring the Distortion of Photographic Objectives

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Received 7 March 1963.

The usual methods of evaluating the radial distortion of photographic objectives provide values for this aberration at discrete points in the field of the objective.[1] It may be desirable, in some cases, to determine the value of distortion continuously across the field. A method of measuring distortion in such a manner was devised, using the phenomenon of moire fringes.

Moiré Fringes. If two fine-line gratings are superimposed, a pattern of fringes is formed. The spacing of the fringes is a function of the period of the gratings and the angle between the gratings (skew angle). (See Fig. 1.)

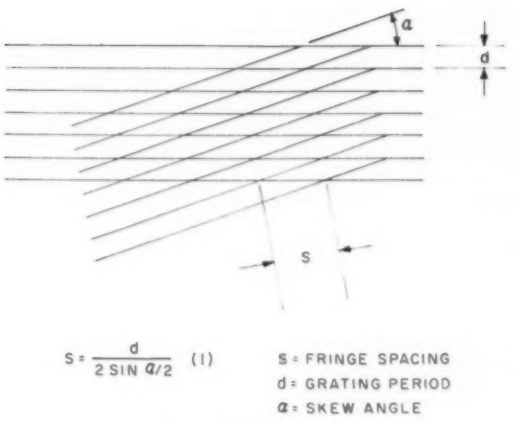

Fig. 1. Moiré fringes.

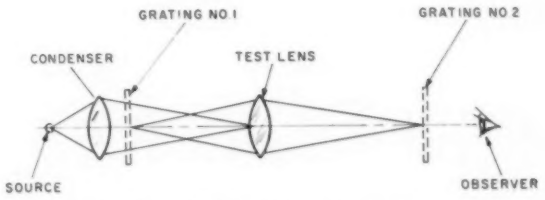

Fig. 2. Schematic of test arrangement.

Description of Method. Grating no. 1 is illuminated and imaged upon grating no. 2 by the objective being tested (Fig. 2). The grating periods and the conjugate foci of the lens are chosen so that the period of grating no. 2 and the period of the image of grating no. 1 are equal. Grating no. 2 is rotated through the angle α, and the pattern of fringes is observed. If the optical system is distortionless, the fringes will be straight, parallel, and equally spaced; if, however, the image is distorted, the fringes will be displaced.

The magnitude of the displacement may be obtained from Eq. (1) (see Fig. 1), holding α constant.

$$\Delta S = \Delta d/(2\sin\alpha/2). \tag{2}$$

Dividing (2) by (1), and solving for Δd, the distortion

$$\Delta d = d\Delta S/S.^{*} \tag{3}$$

The sensitivity of the method is inversely proportional to the grating period. The limiting grating period being, of course, the limiting resolution of the lens. The smallest $\Delta S/S$ which can be measured with accuracy, from a photograph, is about 0.1. It should be possible, therefore, to measure magnitudes of distortion smaller than the limiting resolution of the lens being tested.

This technique may be applied to any optical system used at magnifications of about 6 to about $^1/_6$ simply by substituting appropriate gratings so that the image of grating no. 1 and grating no. 2 have the same period.

* The exact expression is: $\Delta S/S = (\Delta d/d) - (\cot\alpha/2)/(2)\ \Delta\alpha$, which must be used for distortion which is of such a nature as to cause curvature of the imaged grating lines of a magnitude to make $(\cot\alpha/2)/(2)\ \Delta\alpha$ not small relative to $\Delta d/d$. In the experiment described $\Delta\alpha = 0$, and Eq. (3) holds.

In order to test lenses at object distance equal to infinity, a collimator is used. The distortion of the collimator must, of course, be known. The distortion may be determined either by usual methods, or by testing three collimators against each other and determining the distortion introduced by each, as in testing optical flats for flatness. The same precautions regarding total magnification, as previously noted, should be observed.

The principle of the method was demonstrated by a simple experiment. Two 4 line/mm gratings (d = 0.25 mm) and a 5.0-cm focal length enlarging lens, used at unity magnification were arranged similar to Fig. 2.

The photograph of the fringes (Fig. 3) shows very little distortion (less than $^1/_{10}$ fringe) present in the system.

Distortion was introduced into the system by inserting a microscope slide cover glass into the optical path (Fig. 4). The deviation of the fringes is shown, in Fig. 5, to be $^1/_4$ fringe.

From Eq. (3) we obtain:

$$\Delta d = 0.063 \text{ mm}.$$

The deviation produced by a plane parallel plate is given by[2]:

$$Y = t \sin i \left(1 - \frac{\cos i}{n \cos r}\right), \tag{4}$$

where

$Y = \Delta d$,
$i = 45°$, the angle of incidence,
$n = 1.5$, the index of refraction of the plate,
$t = 0.2$ mm, the thickness of the plate, and
$\sin r = (\sin i/n)$

so that

$$\Delta d = 0.066 \text{ mm}.$$

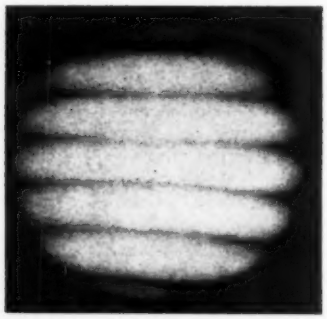

Fig. 3. Photograph of moiré fringes produced by arrangement of Fig. 2.

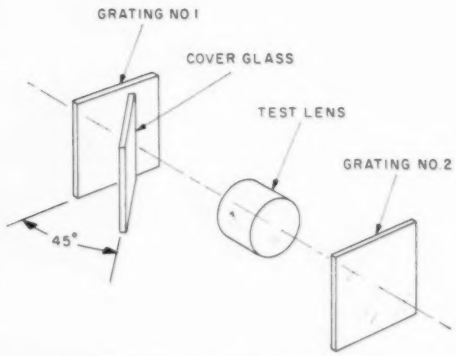

Fig. 4. Method of introducing a deviation of a portion of the image.

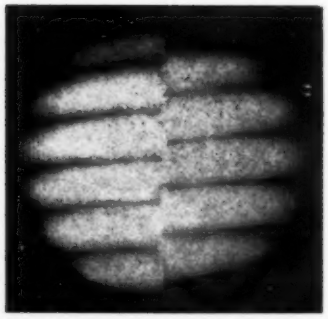

Fig. 5. Photograph of moiré fringes with a deviation introduced as in Fig. 4.

The use of grating with smaller periods would enable measurements to be made with more accuracy than is indicated by this demonstration.

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A Liquid Nitrogen Dewar Attachment for Infrared Detectors

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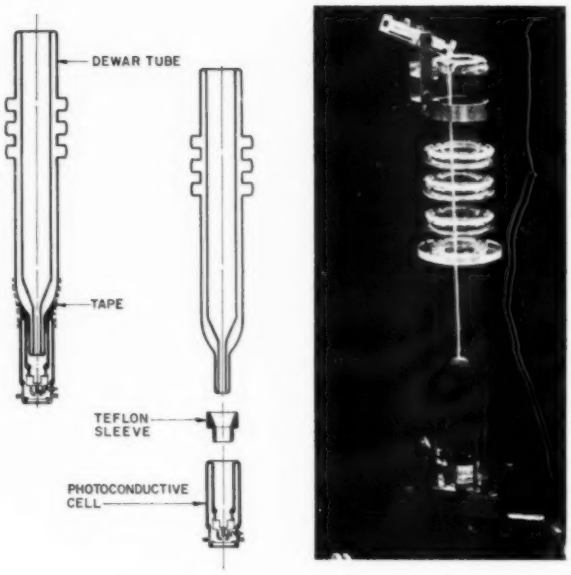
Received 1 April 1963.

A simple addition to cooled infrared detectors is described which increases the capacity of the coolant reservoir. Many of the new cooled infrared semiconductor detectors come equipped with a small dewar which when filled with liquid nitrogen will last approximately 10 min. These detectors are designed to be used with a Joule–Thomson type gas liquifier or some continuous direct liquid nitrogen transfer device. However, with the simple addition of a long dewared-tube extension which is shown in Fig. 1(a), the liquid nitrogen capacity can be increased to approximately one hour before refilling of the reservoir is necessary. For laboratory use where liquid nitrogen is readily available, the addition of a dewared tube to the detector cell is a practical solution to the cooling problem and thus eliminates the need for more expensive and complicated cooling systems.

Figure 1(a) shows a schematic of the detector (in this case a Westinghouse Au-doped germanium cell) dewared extension-tube, and Teflon sleeve. Because of the large difference in area between the two ends of the dewared tube, a bellows was formed on the outside glass wall to relieve any thermal strain on the narrow ring seal. Without the bellows the small ring seal always cracked when the dewar was cooled. The Teflon sleeve is used to center and support the dewared tube on the detector's dewar. Possibly other soft material could be used for the sleeve. There is some contraction due to cooling the sleeve; therefore, the sleeve is made to fit loose. The joint between detector and tube is made gas-tight with Teflon or cellophane tape. It is important to make this seal gas-tight, otherwise the system does not function properly. When the assembled device is filled with liquid nitrogen, it is this gas-tight seal which prevents the liquid nitrogen



(a) (b)

Fig. 1. (a) Schematic diagram of dewar attachment for infrared detectors. (b) Photograph of assembled dewar and detector.

from getting in contact with the joined area by always keeping an insulating jacket of gas between the liquid and the Teflon sleeve. The sleeve and joint area introduce the largest heat leak. The boil-off gas cannot escape at the joint but must travel up the dewared tube.

The actual assembly is shown in Fig. 1(b). The detector is shown at the exit of a monochromator which is being used in shock-tube radiation experiments. The cork float is used to turn the detector bias off when the liquid nitrogen gets too low.

"Bent Axis" Focusing Mirrors

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Received 8 February 1963.

Concave mirrors have an advantage over lenses in optical systems that direct light from a source, through various devices, to a photocell where it is to be measured. The advantage is that there is no chromatic aberration. Hence, the system may be lined up and focused with visible light with certainty that it is then properly adjusted for all wavelengths. An achromatic lens merely has a folded spectrum such that, for example, the focal length for the Fraunhofer C line is the same as for the F line. The adjustment for a wavelength such as 2 μ may be very different. A second advantage is that lenses tend to be opaque in various regions of the spectrum. Ordinary glass gives trouble beyond 2 μ and also in the ultraviolet.

The largest disadvantage of concave spherical reflectors is that the image space interferes with the object space. To overcome spatial interference we have made some mirrors with nonspherical surfaces, so designed that the image space axis is about 90° from the object space axis. This would seem to be a very practical device for more general optical use. Hence, we will start by studying the nature of such a mirror.

Let us consider light from a source at a distance p from the mirror in Fig. 1. This light strikes the mirror and is deviated at an angle φ from its original direction and is focused at a distance q from the mirror. If the object point is considered to be at one focus of an ellipsoid of revolution and the image point at the other, we know that if the mirror coincides with the ellipsoid it will reflect all rays from the object falling on its surface and redirect them to the image. Hence, we can approximate the ideal mirror by one in which the long radius of curvature R (in the plane of the object and image axis) is equal to that of the ellipsoid at point C of the mirror and the short radius r (in a plane perpendicular to the object and image axes) also is the same as the corresponding ellipsoid radius at point C.

By differential calculus we then derive these radii and, hence, the following relations:
If

$$\frac{1}{p} + \frac{1}{q} = \frac{1}{f}, \tag{1}$$

then

$$R = 2f/\sin(\varphi/2), \tag{2}$$

$$r = 2f \sin(\varphi/2), \tag{3}$$

$$\sin^2(\varphi/2) = r/R, \tag{4}$$

$$f = 1/2\sqrt{Rr}. \tag{5}$$

If the cross section of the beams is to be round, the mirror will be an ellipse of axes w and W where

$$w = W \sin(\varphi/2). \tag{6}$$

We turn now to the problem of producing these reflectors. Equation (6) suggests that a flat elliptical disk of axial ratio $\sin(\varphi/2)$ should be used as a tool to be ground into a larger plate. This tool is made from window glass and is ground to shape entirely by eye. Experience shows that if the tool is on the bottom, the overhang will round it off as the upper plate is translated about over it with abrasive between them. Also if the tool is smaller than the $w \times W$ ellipse finally to be produced, the rounding action will be faster. We find that making the tool $^4/_5$ as large as the mirror is good. As the grinding proceeds we check the two radii with a spherometer, made from a dial gauge. If one radius proceeds faster than the other, we bevel the appropriate edge of the tool to accelerate the slow direction. Also one can

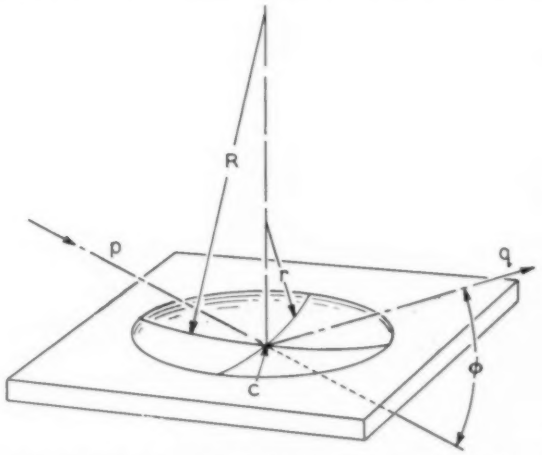

Fig. 1. Relation of two radii of curvature to object and image distances.

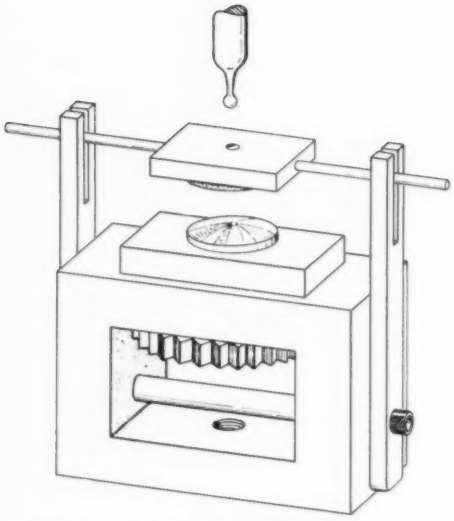

Fig. 2. Optical engine attachment for nonspherical surfaces. The two slotted bars are rigidly clamped to the cross shaft so that they oscillate as one piece. The large knurled thumb screw allows one to secure the tool mounting block to the frame in the desired orientation.

make a few strokes by hand in the slow direction to help this direction catch up.

The machine used is one described by the writer [W. L. Bond, Rev. Sci. Instr. **33,** 372 (1962)], but almost any optical machine would do. An attachment, Fig. 2, keeps the grinding motion always translation of work over tool, never rotation of one relative to the other.

Strictly speaking, only spheres can be ground together fitting in all positions, or cylinders, fitting in all parallel axes positions, but for small motions quite deep curves can be produced by parallel axis sliding. We have made them with $w \times H = 17 \times 24$ mm, with focal lengths 19 mm to 240 mm.

After grinding the desired values of R and r into the glass finer grades of abrasive are used, then the tool is covered with pellon* and the reflector polished with barnesite. The polished reflector is then metal-coated by evaporation. Aluminum is generally used for this coating.

An Interferometer for Precision Angle Measurements

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This work was supported by grants from the Swedish Atomic Research Council.

An angle measuring interferometer of the Michelson type has been constructed for use primarily with a gamma-ray diffraction spectrometer. The interferometer, which has a sensitivity of 0.1 sec of arc on a measuring range of 30° is designed with plane mirrors as end reflectors and a cube corner prism as the movable unit according to principles given by Murty.[1] The moving cube corner prism is mounted fixed relative to the axis, the rotational angle of which is to be measured.

The system is shown in Fig. 1. Behind the beam divider D_2 the cube corner prisms C_1 and C_2 direct the beams toward the end mirrors M_1 and M_2. The prism C_1 which forms the movable unit turns about the axis of rotation 0. C_1' and C_1'' are the positions of the prism at maximum rotation from the central position. The parallel plate P serves as a compensating plate for D_2 and the cube corner prism C_2 compensates the prism C_1.

A semireflecting parallel plate D_1 is placed in the light beam leaving the collimator. One-half of the light flux is thus reflected out of the system while the other half enters the interferometer. After reflection in the end mirrors and interference in the dividing plate D_2, one-half of the returning light flux is reflected in the dividing plate D_1 and directed towards the lens L_3. A third semireflecting parallel plate, D_3, is placed behind the lens L_2. The fringes at infinity are focused on the focal planes of the lenses L_2 and L_3, that is at F_2, F_2', and F_3.

As is pointed out by Peck and Obetz,[2] the fringe patterns at F_2 and F_3 show a relative phase shift which can be used for a direction sensitive photoelectric fringe counting. The pattern at F_2' is used for a visual control of the form and centering of the interference pattern.

In order to obtain a sensitivity of 0.1 sec of arc by counting whole fringes, the radial position of the rotating prism has to be approximately 300 mm from the axis of rotation when green light is used.

The interferometer operates with a continuously varying glass compensation. Due to the large angles of rotation this variation must be considered at the angular calibration of the system. The dependence of the optical path difference on the angles of adjustment of the interferometer components has been derived to a third-degree approximation. The effect of the prisms is analogous to that of twice-traversed parallel plates and hence, as is pointed out by Murty,[1] the center of the fringe pattern remains stationary in the field of view during the rotation. The end mirrors and the beam divider are mounted fixed to the interferometer table; their adjustment is not affected by the rotation.

Within the basic principles of the interferometer several geometrically different arrangements of the components are possible. Different alternatives may give the interferometer different properties from an optical point of view as well as in respect to the measuring accuracy. If both prisms are mounted

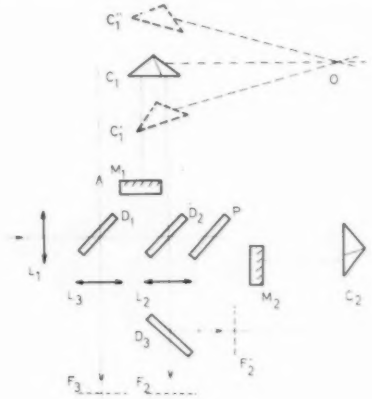

Fig. 1. D_1, D_2, D_3: dividing plates; P: compensating plate; C_1, C_2: cube corner prisms; M_1, M_2: plane mirrors; L_1: collimating lens; L_2, L_3: focusing lenses; F_2, F_2', F_3: focal planes of L_2 and L_3; 0: axis of rotation.

* Geoscience Instruments Corp., 110 Beekman Street, New York, New York.

fixed relative to the axis of rotation the variation of compensation is considerably reduced. If both of the prisms follow the rotational motion and the end mirrors are mounted with parallel normals, the system is insensitive to radial play in the bearing of rotating pivot.

By use of the beam from the light source which is reflected in the dividing plate D_1, the range of the measuring system may be extended by steps. This beam may enter a second interferometer, similar to the primary one and with a measuring range starting where the range of the first interferometer ends. If each interferometer covers a range of 30°, this can be achieved by mounting cube corner prisms at a relative angular position of 60° on a circular table which is fixed to the axis of rotation, and by separating the central positions of the two interferometers by an angle of rotation of 90°. By use of six prism positions on the rotating table the measuring range becomes 360°.

The cube corner prisms of the interferometer may be replaced by trihedral mirrors. This would lead to a considerably simplified angular calibration of the measuring system.

References

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An Image Inverter for Spectral Projector Comparator

Edwin S. Hodge and Edward C. Horey, Jr.

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Received 16 February 1963.

Several manufacturers of spectroscopic apparatus build spectrum projection comparators so that sample spectra may be easily studied by an adjacent master spectrum on a transparent screen. Some instruments and master plates are designed so that the master image is at the top of the screen, while on others the master spectrum is on the lower portion of the screen. If one has a master spectrum for a spectrograph to be used in the projector comparator which reverses the master film layout, the effectiveness of the film is diminished.

In the event of nonavailability of a master spectrum of proper display for a different comparator, the master spectrum can be turned upside down but the legend is inverted [Fig. 1(a)]. Preliminary observations with several prism shapes indicated that it was possible optically to invert the symbols and numerals so that the master spectrum could be used conveniently in its intended manner [Fig. 1(b)]. The construction of such a device is described.

Two modified dove prisms 27.6 cm long were cut from methyl methacrylate sheeting 9.5 mm thick. Using Snell's refraction laws and the index of refraction for acrylic plastic (N = 1.489), the base to height ratio for a dove prism was calculated to be approximately 4.3 (Fig. 2).

A prism height of 9.5 mm and a base length of 3.8 cm produced very satisfactory inverted images of letters and numerals 5 mm high on the screen. The design and construction data for the prism are shown in Fig. 2. The use of two such prisms placed base to base inverts the symbol and wavelength into the same pattern as appears on the original film. Three small magnets fastened to each end of the prism support [Fig. 1(b)] are used to hold the prism to two steel strips on each side of the screen. The addition of these strips to the original projector is the only modification required. The use of the magnets for prism attachment allows precise adjustment of the prism position and easy removal of the entire assembly when necessary.

In order to include the entire spectral range on a 51-cm film holder, the spectrum of a master film is cut out and attached to a piece of spectrum analysis No. 1 film base (emulsion removed) by small segments of clear double-faced cellulose tape. In fastening

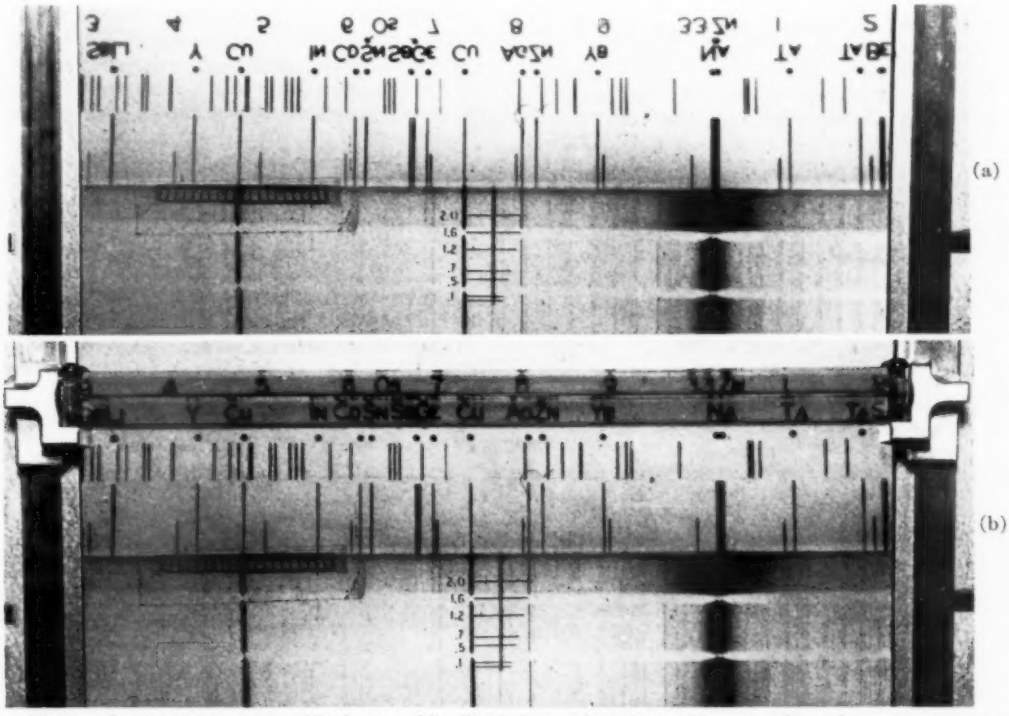

Fig. 1(a). Master film in comparator upside down. (b). Dual dove prisms invert figures and numbers to proper arrangement.

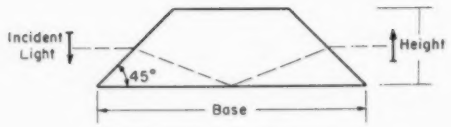

Fig. 2. Cross section of dove prism.

the master strip, it is important that the image edge of the spectrum be aligned exactly parallel to the film edge to eliminate up and down movement of symbols on the screen.

While this system is not perfect, it has proved very satisfactory considering the nonavailability of a master spectrum for mismated spectrographs and projection comparators.

Note on Optical Information Storage in Solids

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Received 25 March 1963.

In a paper on optical information storage in solids [P. J. van Heerden, Appl. Opt. **2**, 393 (1963)] the author calculated the information storage capacity of an alkali halide crystal in a particular case to be about 10^{13} bits per cm^3. Although this figure is correct, it is somewhat misleading by itself, because in actual cases this capacity cannot be fully taken advantage of. In general it can be shown that the efficiency of information storage goes down with the square root of the number of instalments (separate pictures) in which the information is put in. As an example, take a crystal of 1 cm^3, with 10^{15} color centers. Assume that we want to store 3000 pictures of 1 cm^2 each. There will now be available 3×10^{11} color centers per picture. When each picture is defined by 10^8 waves of independent directions, the computation analogous to the one in the paper leads to a signal-to-noise ratio of unity. The amount of information stored is now $3000 \times 10^8 = 3 \times 10^{11}$ bits. This number at the same time gives the theoretical maximum to which the optical storage capacity of the crystal could be utilized.

A White-Type Multiple-Pass Absorption Cell of Simple Construction

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In this letter a multiple-pass White-type absorption cell[1] will be described in sufficient detail so that it could be constructed in a university or industrial workshop using standard pipes, gears, and other parts. The cell features a novel mirror tilt mechanism of simple construction which is different from the mechanism described by Lord.[2]

The cell has been constructed in this laboratory having dimensions similar to White's original cell as described in ref. 1. It has a mirror separation of 61 cm, 3.8-cm long slits, and a semicircular aperture of 7.6 cm. It thus has a minimum f number of 8. In order to simplify the shop work, the cell was not designed for minimum volume as discussed by Edwards.[3]

The tall aperture provided by the semicircular split mirrors was used to advantage, for the cell is used to illuminate the 7.5-cm long entrance slit of an $f/20$ infrared echelle spectrometer.[4] The cell has a large enough product of slit height times numerical aperture to be used with small commercial prism or grating instruments of large numerical aperture and short slits, as well as with specially built high-resolution instruments. For most applications, best results will be obtained using a field lens (or the mirror equivalent) either near the spectrometer slit or in place of one of the cell windows.

Field lenses of NaCl or KBr can easily be ground and polished in any laboratory equipped to prepare infrared cells. The procedure used in this laboratory is first to obtain matching convex and concave glass or metal tools of the desired radius of curvature. Only one polishing lap and one pair of grinding tools are needed if equiconvex lenses are used. The tools should be about $1^1/_2$ or twice as large as the work. The concave tool is used to grind the salt. The convex tool is used to press the polishing lap and to keep the concave tool spherical, for a slight amount of glass will be removed in the preliminary grinding. Salt grinds and polishes very rapidly and need not be fine ground. An abrasive as coarse as 320 carborundum in a salt-saturated solution of about 50% water and ethanol is satisfactory for the fine grinding. However, a more precise surface can be made using fine emery. Polishing is done with very soft pitch and a suspension of levigated alumina in water and alcohol. A piece of the string-mesh bag in which oranges are sold is used to score the lap. The convex tool also can be used to grind to curvature the end of the tube to which the lens will be cemented or waxed. The polished lenses can usually be maintained in satisfactory condition by very light buffing with chamois skin or Kleenex with an ethyl acetate or acetone suspension of levigated alumina or rouge when they become fogged.

Since the cell was constructed using American gears, screws, pipes, and other parts, optical and machine shop dimensions will be given in English units.

The mirrors in the cell were made from 6-in. pyrex blanks using the same tool to provide identical radii. The split objective mirrors were cut in half (without a part way pre-cut) after the polishing had been finished. A small amount of glass has been ground away at opposite ends of a diameter of the field mirror to provide 2-in. long straight parallel edges where the beams enter and leave.

The optical system is contained in and supported by a 32-in. long piece of steel pipe of $7^1/_2$-in. i.d. as shown in Fig. 1. The vacuum seal at the end plate is made using a gasket cut from $^1/_{16}$-in. thick rubber sheet. The end plates are made from $^1/_2$-in. thick boiler plate (hot-rolled steel). The only machined surfaces on the end plates are circular grooves about $^1/_8$ in. deep and wide enough so that the ends of the pipe will fit loosely into them. The gasket goes into this groove and seals against the end of the pipe, which has been turned smooth in a lathe. This method of applying end plates to pipes was shown to us by Dr. Rank. It is as satisfactory as the use of O rings but requires about $^1/_3$ as much machine work. The ring to which the end plate is bolted needs only to be "tacked" in place with an electric arc welder. The in-

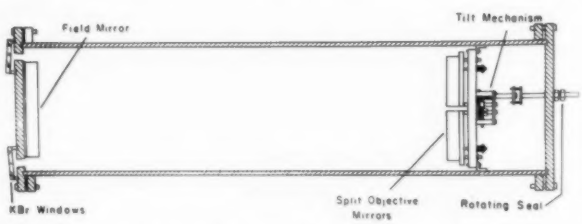

Fig. 1. The White multiple-pass cell.

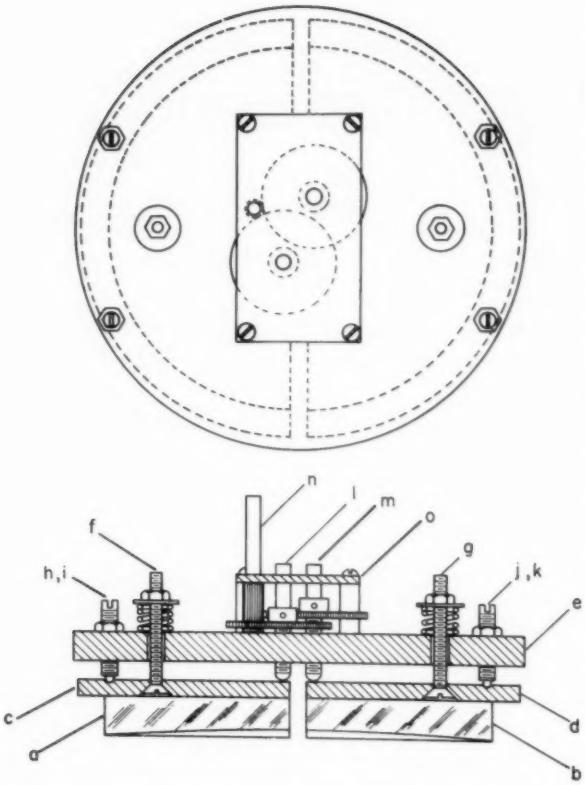

Fig. 2. The tilt mechanism. The pinion on the shaft, n, causes screws l and m to turn against the mirror mounting plates.

ner surfaces of the pipe and plates have been scraped free of loose scale and coated with clear glyptal varnish baked with heat lamps.

The field mirror is supported on an end plate without provision for adjustment. Brass tubes, $^1/_2$-in. long, 2-in. diam, cut at an angle and silver-soldered to the end plate support the cell windows which are cemented to them with glyptal.

The objective mirror tilting mechanism is shown in Fig. 2. The split mirrors a and b are mounted on semicircular plates c and d. These plates are drawn to a circular plate e by means of springs and machine bolts f and g. Part of the flat-headed ends of these bolts have been filed away and the holes in the tilting plates are cut so that the heads will not turn. Each of the semicircular plates is constrained by three screws, h, i, j, k, l, and m. The three screws which determine the position of one of the plates have rounded ends which bear upon a cone-shaped hole, a groove, and a plane surface to provide kinematic restraint. Screws l and m, which are turned in the same direction by the long pinion n, control the number of passes. These screws, which have blunt rounded ends bear upon the plane surfaces. They are constrained from wobbling by bearings in the back plate o. This construction permits adequate control of the mirror position with loosely fitting dry lubricated working parts.

The pinion shaft is turned by means of a commercial double O-ring seal.*

The tilt adjustment screws all have $^1/_4$-28 threads. Screws h, i, j, and k were made from $^1/_4$-in. NF cap screws. Screws l and m were die cut on stainless steel rods. Fifteen-tooth drawn pinion wire and a 48-tooth brass 32-pitch spur gear were used.

The cell provides eight different path lengths from 2.54 to 20.32 meters. The path length is set by means of a single control which is connected to a revolutions counter. The cell described in this letter was constructed several years ago and has proved mechanically and optically reliable for the study of the high-resolution absorption spectra of noncorrosive gases.

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2. R. C. Lord, R. S. McDonald, and F. A. Miller, J. Opt. Soc. Am. **42,** 149 (1952).
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* Consolidated Vacuum Company, Type SE2706. It has a $^1/_4$-in. shaft and is tapped for $^1/_4$-in. national pipe threads.

Papers to appear in subsequent issues

Overhauser and Jeffries-Abragam Effect in a Four-Level System —*Narchal and Barker*

Spurious Harmonic Generation in Optical Heterodyning—*Cummins, Knable, and Yeh*

Interferometric Measurement of Vibration Amplitudes—*Bowie*

Infrared Transmission through Fogged Salt Windows—*Morrow and Turk*

A Simple Grating Calibrator for the Visible and Vacuum Ultraviolet—*Hammer, Arakawa, and Birkhoff*

Photorefractometer II. Measurement of N and K—*Kapany and Pontarelli*

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OSA Around-the-World Group Flight 1964

Revised Information

The International Commission for Optics Symposium on Photographic and Spectrographic Optics will be held in Tokyo 1–8 September 1964, preceded by a Conference on Interference and Coherence convened under the auspices of the ICO and the Australian Academy of Science in Sydney, 23–29 August 1964. The airlines have recently approved an around-the-world group flight fare for 15 persons or more, and OSA, even at this early date, is interested in learning the number of members who are potentially interested in attending these two meetings and participating in this group flight. It is also hoped to have an informal gathering in Israel (say 13–17 August), and perhaps something similar in India (say 18–19 August). It appears better for our purpose to finish this around the world trip in the Orient (rather than to start it there as had been our original intent), so our revised—but still tentative—schedule now looks like:

		From	To	Purpose
Aug. 8	lv. 10:00 pm	NYC	London	
9	arr. 9:35 am		London	
11	lv. 11:55 am	London	Athens	
	arr. 4:20 pm		Athens	
13	lv. 7:20 pm	Athens	Tel Aviv	informal colloquium?
	arr. 9:20 pm		Tel Aviv	
17	lv. 9:25 pm	Tel Aviv	New Delhi	
18	arr. 9:10 am		New Delhi	
19	lv. 12:15 pm	New Delhi	Bangkok	
	arr. 5:15 pm		Bangkok	
21	lv. 6:05 pm	Bangkok	Singapore	
	arr. 8:40 pm		Singapore	
22	lv. 9:30 pm	Singapore	Sydney	
23	arr. 9:35 am		Sydney	ICO Interference and Coherence Meeting—(Sessions 24–25, visits to lab. 26–27, visits outside Sydney 28–30)
31	lv. 10:05 am	Sydney	Tokyo	
31	arr. 11:40 pm		Tokyo	
Sept. 1–8				ICO Mtg. Tokyo & Kyoto on Photographic and Spectroscopic Optics
8	lv. 11:15 pm	Tokyo	Honolulu	
8	arr. 11:40 am		Honolulu	
10	lv. 11:30 pm	Honolulu	San Francisco	
11	arr. 7:15 am		San Francisco	
11	lv. 8:30 am	San Francisco	New York	

The group fare would be approximately $1150 economy class round trip. Only OSA members and their immediate relatives may participate. Would members who are potentially interested (there is no commitment) fill in and return this form. The interest of those who have already written in is recorded.

Assistant Secretary, OSA
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1155 Sixteenth Street, N.W.
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REPLY

I am interested in principle in participating in the OSA 1964 AROUND-THE-WORLD GROUP FLIGHT, and I wish to have information as it becomes available.

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Address.....

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The Publications of W. W. Coblentz on Infrared Spectroscopy

The principal work of the late W. W. Coblentz on infrared spectroscopy originally appeared in three Publications of the Carnegie Institution of Washington. Publication No. 35, issued in 1905, dealt with his investigations at Cornell University of the infrared absorption spectra of some 135 organic compounds, with shorter supplementary sections on transmission and reflection spectra. Publication No. 65 (1906) and Publication No. 97 (1908) are concerned with later work on the transmission and reflection spectra of minerals and other inorganic compounds carried out at the U.S. Bureau of Standards.

These classical investigations form the basis of most modern work on analytical infrared spectroscopy. The journals have long been out of print, but, with the kind permission of the Carnegie Institution, they have recently been reprinted in a single volume under the joint sponsorship of the Coblentz Society and the Perkin-Elmer Corporation.

All concerned with modern applications of infrared spectroscopy to problems of chemical structure and analysis should be conversant with this early work, which provides the basis for much of the modern technique. To maintain a properly balanced outlook on the subject, this volume should accompany the standard modern texts on the library shelf of the spectroscopy laboratory.

A limited number of copies of the first reprinting are still available at $3.50 per copy on application to Dr. H. B. Kessler, The Secretary, c/o The Perkin-Elmer Corporation, Norwalk, Connecticut.

From left to right: Thomas B. Dowd *ONR Boston*, Sidney Passman *Rand Corp.*, Max Garbuny *Westinghouse*, Lloyd G. Mundie *Lockheed*, Raymond H. McFee *Aerojet-General*, Warren E. Mathews *Hughes*, and Robert M. Talley *Santa Barbara Research Center*.

From left to right: Jay Froman *ONR San Francisco*, Eric M. Wormser *Barnes Engineering*, Werner K. Weihe *ERDL*, Chester Pierce *Air Force Systems Command*, Henry Bisschop *U.S. Army Security Agency*, and Herbert Friedman *Naval Research Lab.*

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Scope: Papers are welcomed in the broad areas of applied optics, in disciplines related to optics and employing optical techniques. Papers should be sent to *The Editor, APPLIED OPTICS, 1155 Sixteenth St. N.W., Washington 6, D.C.* Manuscripts may be submitted in English, French, German, or Russian, and the presentation should be as succinct as comprehension will permit. In general, the metric system of units is preferred. One original and one carbon copy of the manuscript, with two sets of all illustrations, must be sent in. Manuscripts should be typed double or triple spaced on one side of 22 × 28 cm (8½ × 11 in.) paper, leaving a 3.8 cm (1½ in.) margin all around. Equations must be typed not hand written wherever possible. Papers on the more fundamental aspects of experimental and theoretical optics should be sent to *The Editor, JOURNAL OF THE OPTICAL SOCIETY OF AMERICA, National Bureau of Standards, Washington 25, D.C.*

An **abstract,** adequate as an index and a summary, of not more than 100 words should appear at the beginning of the paper after the *title, author's name, affiliation, and address.* In the case of papers in a non-English language, they must be accompanied by an abstract in English as well as an abstract in the language of the paper. It should be borne in mind that this abstract may be used in toto by the abstracting journals, therefore it should be self-contained.

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2. J. Culpeper, *Space Optics* (Georgetown Institute of Technology Press, Washington, D.C., 1861), pp. 12, 345.

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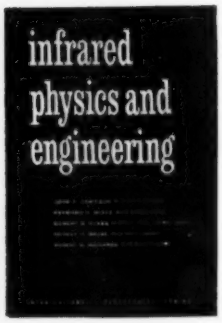

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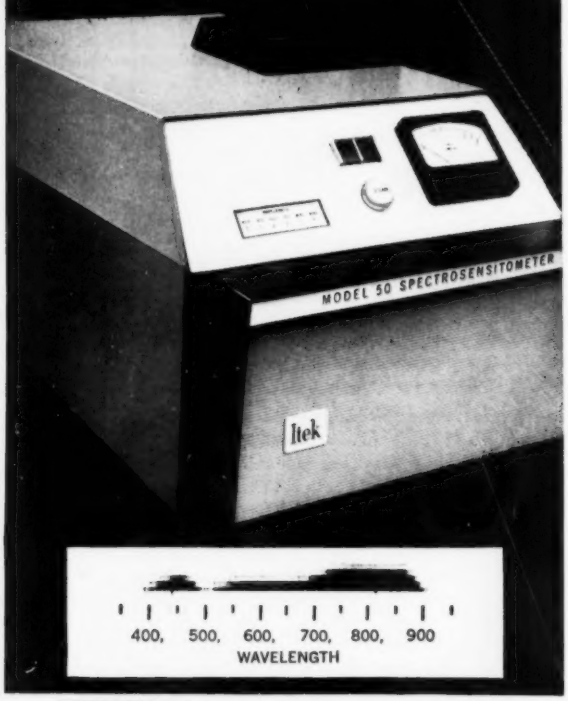

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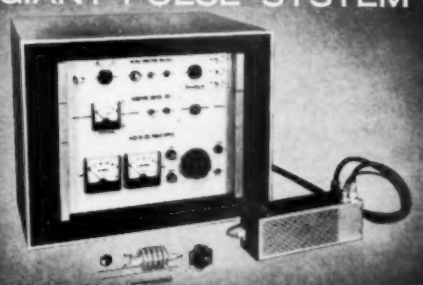

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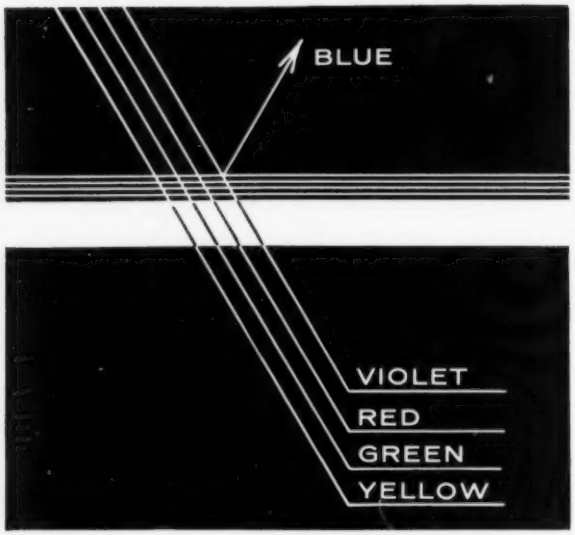

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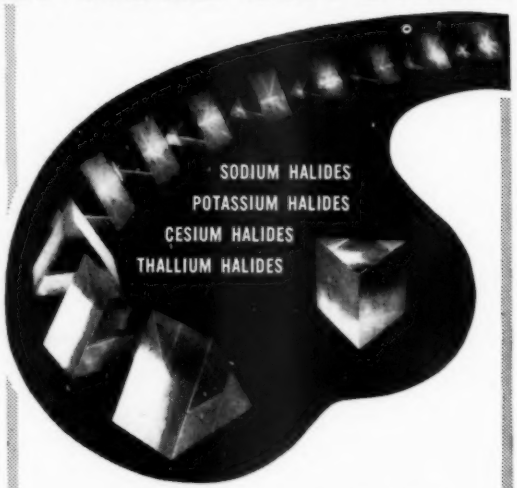

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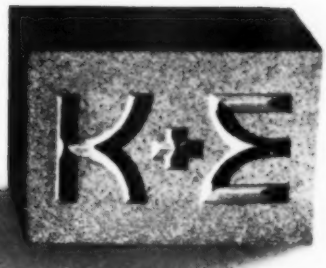

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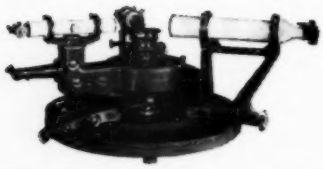

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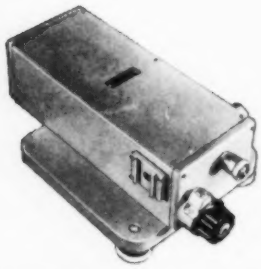

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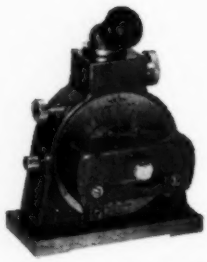

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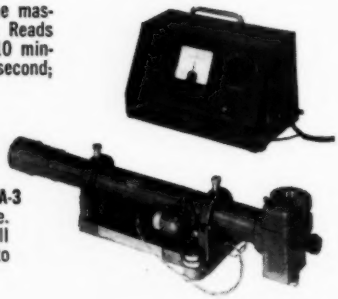

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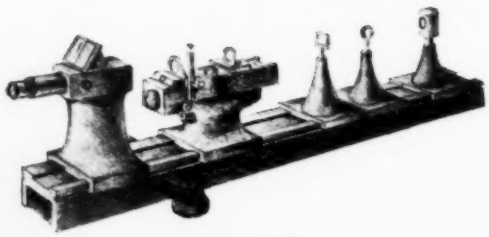

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